

A STUDY OF SULFUR AND SELENIUM CONTAINING LIGANDS

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BECK YU TAN



A STUDY OF SULFUR AND SELENIUM CONTAINING LIGANDS

by



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A Thesis submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy

Department of Chemistry
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February 1975

St. John's

Newfoundland

ABSTRACT

The substituted (arythio)-, (arylseleno)- and (arylsulfoxy)-acetic acids, $RC_6H_4YCH_2CO_2H$ ($Y = S, Se, SO_2; R = H, m, p-CH_3$) are studied as ligands towards Pt(II), Pd(II) and Cu(II) ions. The thio and seleno ligands $RC_6H_4XCH_2CO_2H$ ($X = S, Se$) form bis-complexes, ML_2 , with Pt(II) and Pd(II) whereas the sulfoxy ligands ($Y = SO_2$) form only complexed ions $(MLX_2)^-$ with Pt(II) and Pd(II) (where $X = Cl, Br$).

The bis-complexes of platinum(II) and palladium(II) are coordinated via the thio or seleno group and the carboxylate group of the ligands. The assignment of trans structure is based on the non-coincidence of the ν_{M-O} and ν_{M-S} bands in the infrared and Raman spectra and also from steric consideration. In these bis-complexes, chelate formation causes magnetic inequivalence of the methylene protons in the 1H n.m.r. spectra. In addition the presence of chiral centers at sulfur or selenium atoms results in the observations of two sets of methyl and methylene absorptions which coalesce at high temperature. This phenomenon of the 1H n.m.r. spectra indicates the co-existence of the diastereoisomers (meso and dl).

(Arylsulfoxy)acetic acid is a potential ambident ligand. In the sulfoxy complexed ions $(MLX_2)^-$ the sulfoxy group utilizes the sulfur atom in bonding. The effects of chelation and strong electron withdrawing ability of the sulfoxy group render the methylene protons acidic.

For the bis-complexes of copper(II), CuL_2 , ($Y = S, Se; R = m$ or $p-CH_3$), whether the S or Se atoms participate in the chelate formation is still not clear.

ACKNOWLEDGEMENTS

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The author wishes to express her sincere gratitude to Drs. M. J. Newlands and N. J. Gogan for their supervision and many helpful suggestions. I am grateful to Mr. E. Benson for recording the variable temperature ¹H n.m.r. spectra and to Dr. V. Salares for recording the Raman spectra. Thanks are also due to the Geology Department of Memorial University of Newfoundland for recording the X-ray powder diffraction patterns. A fellowship from the Chemistry Department of Memorial University of Newfoundland and financial assistance from the National Research Council of Canada are gratefully acknowledged. Finally, special thanks must also go to my husband, Ping-teng, for his enthusiastic encouragement.

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CHAPTER I

GENERAL INTRODUCTION

Recent researches on coordination chemistry have revealed the wide occurrence and good coordinating properties of sulfur- and selenium-containing ligands.¹ A large number of various types of sulfur-containing ligands, a lesser number of selenium- and a few of tellurium-containing ligands have been reported. These include the sulfide and selenide ions (S^{2-} , Se^{2-}), thiols (RS^-), thiocyanate (SCN^-), selenocyanate ($SeCN^-$), thioether (R_2S), selenoether (R_2Se), thiourea (NH_2CSNH_2), selenourea (NH_2CSeNH_2), thioacetamide (CH_3CSNH_2), triphenylphosphine-sulfide and selenide ($C_6H_5)_3P=X$, where $X=S, Se$), sulfoxide (R_2SO), sulfite ion (SO_3^{2-}), etc.¹

The coordinating properties of the various types of sulfur- and selenium-containing ligands may be quite different. For instance, the polarisabilities of sulfur ligands decrease in the order $S^{2-} > RS^- > R_2S > R_2SO$. It is thiols rather than thioethers that cause spin-pairing in complexes of $Co(II)$ and $Ni(II)$.² The coordinated thiol complex is able to act as a ligand by donating a second pair of electrons from the sulfur atom. Thus, bis-ligand complexes of 2-aminoethanethiol with $Ni(II)$ and $Pd(II)$ react with the corresponding metal salt to yield a trimeric complex.³ The structure of the nickel complex has been confirmed by x-ray diffraction (see Fig.1).⁴ Not only the polarisabilities of sulfide ion, thioether and sulfoxide decrease in that order, but the number of lone pair electrons in this series of ligands also decreases in the same order, viz., $S^{2-} > RS^- > R_2S > R_2SO$. It has been suggested that the coordinating properties of thiols and thioethers are different because thiols are more

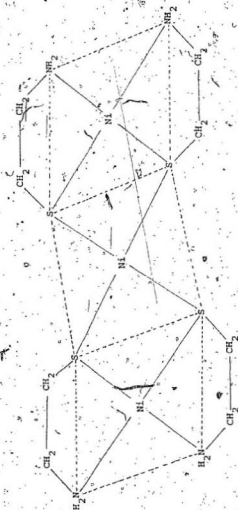


Fig. 1 Structure of trimeric nickel complex



highly polarisable than thioether but are not as effective d_{π} -acceptors as the latter.⁵

The present investigation was concerned with carboxylic acids with sulfur- or selenium-containing substituents. The compounds concerned were substituted phenylthio-, phenylseleno- and phenylsulfoxy-acetic acids of general formula $RC_6H_4XCH_2CO_2H$ (where $R=H$, $o-CH_3$, $m-CH_3$, $p-CH_3$, $X=S$; $R=H$, $p-CH_3$, $X=Se$; $R=m-CH_3$, $p-CH_3$, $X=SO$). It is necessary, therefore, to compare the parent acids and some of their related complexes before proceeding further.

The general properties of the ligands and their known related complexes are reviewed briefly. A short account of some related concepts are also presented here.

The acid dissociation constants of the parent acids and some related compounds are located in Table 1.

Table 1
Acid Dissociation Constants (pK_a) of $RC_6H_4XCH_2CO_2H$ at $20^\circ C$ ^{6,7}

| | $X=CH_3$ | $X=O$ | $X=S$ | $X=Se$ | $X=SO$ | $X=SO_2$ |
|----------|----------|-------|-------|--------|--------|----------|
| $R=H$ | 4.66 | 3.17 | 3.38 | 3.75 | 2.73 | 2.51 |
| $o-CH_3$ | -- | 3.23 | 3.38 | 3.76 | -- | -- |
| $m-CH_3$ | 4.65 | 3.20 | 3.39 | 3.78 | 2.76 | 2.57 |
| $p-CH_3$ | 4.69 | 3.22 | 3.45 | 3.83 | 2.74 | 2.54 |

The Hammett ρ values of $C_6H_5XCH_2CO_2H$ are 0.226, 0.300, 0.166, 0.253 for $X=O$, S , SO , SO_2 respectively.⁷

The acid dissociation constant and Hammett ρ value should be a

measure of the ability of the atom or group X to transmit electronic effects from the phenyl rings to the carboxyl group. The changes in acid strength, ΔpK , when a substituent R is introduced into the phenyl rings in a meta- or para-position can be predicted by the Hammett free energy relationship,⁸

$$\Delta pK = \rho \sigma$$

where σ is the substituent constant.

From Table 1, it is seen that the acidity of $RC_6H_4XCH_2CO_2H$ decreases in the order $O > S > Se$, but increases in the order $S < SO < SO_2$. All of these acids are stronger than the corresponding phenylpropionic acids. The increase of acidity caused by the sulfur-oxygen linkage is particularly large because the highly polar sulfur-oxygen bond has a strong electron-withdrawing inductive effect which is also indicated by the low Hammett ρ value, indicating reduced ability of the sulfoxo group to transmit substituent effects.

It is likely that these differences in acidity should correlate with donor power. The fact that different metals form complexes of differing orders of stability with ligands was discussed by Uhrlund et al.⁹ in terms of class "a" and "b" character. Class "a" metals form complexes such that the order of stability of complexes with group VI ligands, for example, is $O \gg S > Se > Te$, whereas for class "b" complexes the reverse is true. Similar criteria apply to group V and VII ligands.

Pearson modified and extended the classification by using the terms "hard" and "soft" to describe both the Lewis acids and Lewis bases on the basis of their polarisability.¹⁰ Thus, "hard" metal ions (class

"a") are small, highly charged, and bind strongly to the least polarisable (hardest) ligand atom of a group, forming more polar bonds. "Soft" metal ions (class "b") are large, have a low oxidation state, easily distorted outer electrons, and bind best to the "soft" (easily polarisable) ligand atom of a group, forming more covalent bonds. In the case of sulfide S^{2-} ion, however, it is highly polarisable and yet strongly binding to the proton.

These newly developed ideas of "hard" and "soft" acids and bases had been foreshadowed many years ago. Several earlier workers, especially Fajans et al.¹¹ and Bjerrum¹² have noted that the metal ions fall into two categories according to the kinds of bases they prefer to coordinate with.

Ahland has shown that in class "a" complexes entropy effects, ΔS , dominate the thermodynamics, whereas in class "b" complexes, enthalpy effects, ΔH , dominate the thermodynamics.¹³

Inorganic Derivatives

The metal complexes of sulfur- and selenium-containing ligands in general¹ and sulfoxide-metal complexes in particular¹⁴ have been reviewed. The organic selenium- and tellurium-containing ligands have been less extensively studied than the corresponding sulfur ligands.¹⁵

The sulfur and selenium ligands which are "softer" or more class "b" in character are expected to form relatively stable complexes with "soft" metals such as Ag(I), Pd(II), Pt(II), Rh(I), Ir(I), Au(I), etc. Divalent metals of the first transition series are "harder" or more class "a" in character and so would be expected to show a comparatively

smaller affinity for ligands with heavy donor atoms than for those from the first period. Thus, the complexes of some alkylthio-, arylthio-, alkylseleno- and arylseleno-acetic acids with first row divalent metal ions are of low stability.¹⁶ The formation constants indicate that the stability decreases as follows: alkyl > aryl; thio > seleno and Cu(II) > Co(II) > Mn(II) > Zn(II) > Ni(II); with Cd(II) showing variable class "a" and "b" character. That all the "hard" metal complexes are very weak can be seen by comparing their formation constants K_{ML} with those of the silver complexes (Tables 2 and 3).

Table 2
Formation Constants By pH Titration (K_{ML}).¹⁶

| Ligand $R-CH_2CO_2H$ | Ag(I) | Cd(II) | Cu(II) | Ni(II) | Co(II) | Mn(II) | Zn(II) | H ⁺ |
|-------------------------|-------|--------|--------|--------|--------|--------|--------|----------------|
| $R=C_6H_5S$ | 676 | 4.7 | 27 | 2.0 | 5.8 | 5.2 | 2.1 | 2400 |
| $R=C_6H_5Se$ | 4800 | 4.8 | 19 | -- | 4.3 | 2.1 | 4.0 | 5620 |

Table 3
Stability Constants (log K).¹⁷

| Ligand $R-CH_2CO_2H$ | Ag(I) | Pb(II) | Cd(II) | Cu(II) | Ni(II) | Co(II) | Mn(II) | Zn(II) | H ⁺ |
|-------------------------|-------------------|------------------|------------------|-------------------|-------------------|-------------------|-------------------|-------------------|--------------------|
| $R=HS$ | -- | 8.5 ^c | -- | -- | 6.98 ^d | 5.84 ^c | 4.38 ^d | 7.86 ^c | 10.20 ^d |
| $R=C_2H_5S$ | 4.1 ^c | 3.9 ^d | -- | 4.55 ^d | 3.12 ^d | 3.06 ^d | -- | 3.14 ^d | 5.06 ^d |
| $R=C_6H_5S$ | 7.27 ^b | 1.8 ^c | 1.2 ^c | 1.5 ^c | 0.7 ^c | -- | -- | 0.6 ^c | 3.37 ^c |

$$b \quad \beta_2 = \frac{[ML_2]}{[M][L]^2}$$

c. in aqueous medium

d. in 50 % dioxan.

As can be seen from the stability constants, the complexes become weaker in the order $HS > C_2H_5S > C_6H_5S$.

A preliminary study of phenylsulfoxyacetic acid with divalent metal ions indicates that in most cases, the sulfoxy group is not participating in the reaction.¹⁸ In the present work, therefore, only relatively "soft" metal ions have been used and the metal complexes have been isolated to study spectroscopically.

In the present work, substituted arylthio-, arylseleno- and arylsulfoxy-acetic acids, $RC_6H_4XCH_2CO_2H$ ($X=S, Se, SO$), have been studied as ligands toward $Pt(II)$, $Pd(II)$ and $Cu(II)$ ions. This work includes three parts:

- (I) the bis-complexes ML_2 (where $M=Pt(II), Pd(II)$, $L=RC_6H_4SCH_2CO_2^-$ and $RC_6H_4SeCH_2CO_2^-$).
- (II) the sulfoxy complexes $K[M(RC_6H_4SOCH_2CO_2)(hal)_2]$ where $M=Pt(II), Pd(II)$, $hal=Cl, Br$; and
- (III) the bis-complexes of copper(II) with $RC_6H_4XCH_2CO_2^-$ (where $X=S, Se, SO$).

These three types of complexes are discussed in turn in the following chapters.

CHAPTER II

INNER COMPLEXES OF Pt(II) AND Pd(II) WITH ARYLTHIO- AND ARYLSELENO-ACETIC ACIDS

Introduction

The complex salts of platinum and mercury with methylthio-¹⁹ and ethylthio-²⁰ acetic acids were studied long ago. Livingstone *et al.* reported that o-methylmercaptobenzoic acid formed inner complexes with Pd(II), but not with Pt(II).²¹ (Phenylthioacetic acids have been reported briefly to form insoluble salts with Pt(II).²² However, due to the low solubility of this type of complex, few ¹H n.m.r. spectroscopic data are available.

The coordination chemistry of some sulfur-containing amino acids such as cysteine, cystine, glutathione, methionine or penicillamine are of recent interest because of their biological importance.²³ The reaction of a S-containing amino acid with Pt(II) and Pd(II) yields in most cases the chelates using the sulfur and amino group, while the carboxylate group remains uncoordinated.²³ The exception is the complexation of cysteine, $\text{HSCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$, with Pt(II) and Pd(II) in which coordination occurs via S and O in $\text{M}(\text{L-H})_2$ complexes.^{24,25}

A series of organic sulfide and selenide complexes of the type $\text{trans}-(\text{PdX}_2\text{L}_2)$ ²⁵ (where X=Cl or Br, $\text{L}=\text{R}_2\text{S}$, R_2Se) have been studied by infrared and ¹H n.m.r. spectroscopy.

In the study of the stabilities of a series of silver complexes of substituted(phenylthio- and(phenylseleno)-acetic acids, Pettit and his collaborators proposed that for(phenylthioacetic acids (HL) of general formula $\text{RC}_6\text{H}_4\text{SCH}_2\text{CO}_2\text{H}$, the stability of the species AgL , AgHL^+ and AgL_2^-

2

9

tends to increase as the electron-releasing nature of the phenyl substituent of the ligand increases; and to decrease as the substituent becomes more electron-attracting (with the exception of the substituents $R = o\text{-SCH}_3$ and $p\text{-SCH}_3$).²⁶

Since the stabilities of the protonated silver complexes AgHL^+ (where $\text{HL} = \text{RC}_6\text{H}_4\text{SCH}_2\text{CO}_2\text{H}$) vary with the inductive effects of the substituents, the authors suggested that changes in sigma bonding between sulfur and silver atoms are the major factors contributing to the free energy changes observed. Hence, they predicted that the bonding of the phenyl group to the sulfur atom would markedly reduce the stabilities of the complexes relative to the (alkylthio)acetic acid complexes.²⁷

The stability of the silver complexes of substituted (phenoxy-, phenylthio- and phenylseleno-)acetic acids has been shown to decrease in the order $\text{Se} > \text{S} \gg \text{O}$.³ It was concluded that for the substituted (phenylthio- and phenylseleno-)acetic acids, the Ag-L bond is enthalpy-stabilized and the increased stability of the selenium complexes is due entirely to an enthalpy effect.²⁸ The large increase in stability of complexes containing sulfur or selenium as donor atoms over those containing oxygen donor atoms has been attributed to the back donation from filled metal ion d-orbitals to empty ligand d-orbitals.²⁷ These two explanations may be different aspects of the same phenomenon since back donation implies an increase in bond order and, presumably, an increase in enthalpy of formation.

Coordination of a metal ion to the sulfur atom of substituted thioacetic acid is expected to increase the acidity of the acid because removal of negative charge from the sulfur atom would encourage disso-

ciation of the carboxyl proton. The increase in acidity of (phenylthio)acetic acid by 0.76 pK unit on coordination of silver to the sulfur atom is to be expected if the silver-sulfur bond is largely sigma in character. The substitution of a phenyl group on the sulfur atom reduces the stability of the complex considerably and this shows that a reduction in donor capacity of the sulfur atom is not matched by an increase in its π -acceptor capacity.²⁹

Since the physical methods such as ^1H n.m.r., infrared, Raman and electronic spectra are used to characterize the compounds of the present system, a short account of their use in some related systems is given below. Also, the types of isomerism which will be dealt with in the discussion section are given here.

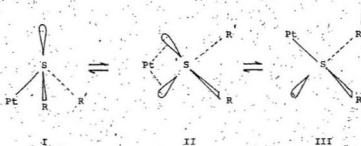
Proton Magnetic Resonance (^1H n.m.r.)

^1H n.m.r. spectroscopy has been employed to study the interaction of some cysteine, $^-\text{S}-\text{CH}_2\text{CH}(\text{NH}_2)\text{COO}^-$, derivatives with metal ions [e.g. $\text{Hg}(\text{II})$]. It is known that the magnitude of the downfield shift per proton is usually the greatest for those protons situated closest to the metal ion (in terms of bond distance). In an alkaline solution, the chemical shifts of the CH and CH_2 groups of the cysteine derivatives experience considerable downfield shifts on complex formation, while in an acidic condition, the effect on CH group is comparatively smaller. This suggests that the ligand, cysteine, acts as a bidentate ligand in an alkaline condition but as a monodentate ligand, bonded only through the sulfur atom, in an acidic condition.²⁴

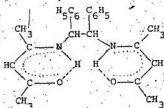
The question of configuration of sulfur in thioether complexes has

been examined by ^1H n.m.r. which indicates that at low temperature the sulfur atoms are pyramidal, but on warming inversion occurs and this pyramidal sulfur averages to a planar conformation.^{30,31, 32} A similar phenomenon was observed for the complexes of a selenium ligand.^{32,33}

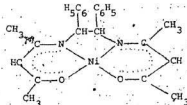
The methylene resonances of cis-bis(dibenzylsulfide)dichloro-platinum(II) are of the AB type. The AB pattern collapses to an A_2 pattern at higher temperature while the Pt-H coupling is preserved. Thus, rapid inversion of configuration at sulfur with retention of the Pt-S bonds at higher temperatures is indicated. A partial bond breaking and bond formation mechanism has been suggested for the inversion:³¹



N.m.r. spectroscopy provides a means of distinguishing between dl and meso isomers as is well illustrated by the spectra of bis(acetyl-acetone)-meso-stilbenediamine, its nickel chelates, and the analogous dl-ligand and Ni(II) chelate (IV and V).



IV



V

Since the pure isomer was obtained in each case, the differences in the ^1H n.m.r. spectra were ascribed to magnetic effects arising principally from the position of the two phenyl groups relative to each other and to the other protons in the molecule.³⁴

The ^1H n.m.r. data of the two isomeric ligands, dl- and meso-acetylacetonate-stilbenediimine, and their nickel(II) chelates are located in Table 4. The meso form has a plane of symmetry perpendicular to the C-C bridge bond while the d and l forms contain no such plane, but are mirror images of each other.

Table 4
¹H n.m.r. Data of Acetylacetone-Stilbenediimine Derivatives
 Chemical shift (ppm)

| Compound | CH ₃ (diketone) | CH (diketone) | N-H...O | CH (of bridge) | C ₆ H ₅ |
|---------------------------------------|-------------------------------|------------------|---------|-------------------|-------------------------------|
| <u>dl</u> ligand (IV) | 2.13 1.80 | 4.99 | 11.73 | 4.72 | 7.14 |
| <u>meso</u> ligand (IV) | 2.12 1.68 | 4.97 | 11.47 | 4.86 | 7.24 |
| <u>dl</u> nickel(II) chelate (V) | 1.93 1.50 | 4.86 | -- | 4.19 | 8.30; 7.40 |
| <u>meso</u> nickel(II) chelate (V) | 1.89 1.53 | 4.87 | -- | 4.66 | 7.56; 7.04 |

In the free ligand, the difference between the dl and meso forms in the resonance of the methyl groups adjacent to the diimine and also the bridging groups is explained as an effect of differences in proximity of the proton to the π cloud of the phenyl group on the adjacent carbon atom. In the dl form, the methyl groups are on the average farther from the phenyl groups and, therefore, are less affected by the π cloud than is the case in the meso form.

In the nickel(II) chelate, the two bridge protons of the meso isomer are adjacent to one another and rather removed from any diamagnetic shielding effects of the phenyl groups. In the dl isomer, on the other hand, each proton is rather strongly shielded by the π cloud of the phenyl groups on the next carbon; the resonance accordingly is more shielded. ³⁴

Vibrational Spectra

Square planar bidentate chelates complexes $M(L-L')_2$ such as bis(glycinato)platinum(II) may exist in cis and trans forms.



cis (C_{2v})

VI



trans (C_{2h})

VII

As required by symmetry, the cis isomer with local symmetry C_{2v} should yield two metal-ligand stretchings for each donor atom, e.g., two ν_{M-O} and two ν_{M-N} while the trans isomer with local symmetry C_{2h} should possess only one ν_{M-O} and one ν_{M-N} in both the infrared and Raman spectra. Furthermore, the trans isomer has a center of symmetry so that the metal-ligand stretching frequencies will not coincide in the infrared and Raman spectra.³⁵

Electronic Spectra

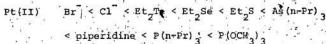
The electronic spectral absorptions of a transition metal complex may arise from the d-d transition of the metal ion, the charge transfer which is associated with a ligand to metal or a metal to ligand charge transfer process, or an intraligand transition.

The elongation along the z-axis of two metal ligand bonds in an octahedral complex results in a tetragonal distortion. In the limit of a very large tetragonal distortion the complex can best be treated as square planar, with only four ligands surrounding the metal atom. Gray notes that the exact order of the d-orbital splitting in a square planar field is not certain, but the d-orbital energy level sequences of

$$dxz, dyz < dz^2 < dxy < dx^2 - y^2$$

is most consistent with results obtained in studies of square planar cyanides and halides.³⁶

For a given metal and stereochemistry, ligands may be arranged in a series according to their capacity to cause d-orbital splittings. From spectra of trans-Pt(L)(piperidine)Cl₂ complexes, Chatt et al. suggested the following spectrochemical series:³⁷



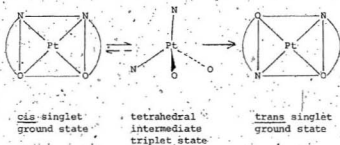
Stereoisomerism

Stereoisomerism is concerned with the spatial distribution of atoms in a molecule. There are three forms which are of direct concern to the present work: geometrical isomerism, optical isomerism and diastereoisomerism.

(a) Geometrical Isomerism

Square planar complexes of unsymmetrical ligands, M(LL')₂, are known to occur as geometric isomers, with the possibility of inter-

conversion of the two forms, cis and trans. Until recently, data for cis-trans isomerization of planar complexes referred only to thermodynamic and photochemical studies. For example, cis-bis(glycinato)platinum(II) upon irradiation of the "d-d" type bands in the near UV, rearranges to the trans isomer with a value of isomerization constant of ca 0.13.³⁸ The reverse reaction, i.e., trans to cis isomerization, does not occur, although prolonged irradiation of the charge transfer band (254 nm) for the trans isomer leads to decomposition.³⁸ An intramolecular twist mechanism (one without bond cleavage) with a tetrahedral intermediate (VIII) has been proposed.



VIII

Cis-bis(glycinato)platinum(II), when heated in the presence of free glycine, converts to the trans isomer.³⁹ It has been suggested that the thermal reaction proceeds via an intermolecular path. Cis-Pt(PET₃)₂-(o-tolyl)Cl is found to undergo isomerization in the absence of any catalyst.⁴⁰

Redfield and Nelson have studied the cis-trans isomerization of $[\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2]_2\text{PdCl}_2$ and $[(\text{C}_6\text{H}_5)_2\text{PCH}_3]_2\text{PdCl}_2$ and found that the ratio of cis to trans isomers was a function of both the solvent and the temperature, and that equilibrium was rapidly established.⁴¹

(b) Optical Isomerism and Diastereoisomerism

Optical isomers (or enantiomers) have structures that are non-superimposable mirror images of each other and are able to rotate the plane of polarization of plane-polarized light. They have identical physical and chemical properties.

A metal complex can gain dissymmetry through (i) the distribution of chelate rings about the central metal ion, (ii) the conformations of the chelate ring, (iii) the coordination of unsymmetrical multidentate ligands, (iv) the coordination of an optically active ligand and (v) the coordination of a donor atom that is asymmetric.⁴² Dissymmetric complexes are optically active, but contain an axis of rotation. For example, the cis-dichlorobis(ethylenediamine)cobalt(III) ion with a C_2 axis is dissymmetric. Diastereoisomers are stereoisomers that have the same elements of dissymmetry, some but not all of which are enantiomeric. An asymmetric complex is entirely void of symmetry.

Conformational Analysis

Conformation is the term used to denote any one of a number of momentary arrangements of the atoms in space that result from rotation about single bonds. Conformational analysis is a method of determining

the relative stability of complexes with different ligand conformations by considering various interatomic interactions.

The bidentate ligands described in this work form five-membered rings with the metal atoms. Different conformations may be formed for the puckered ring. Conformational analysis of the ethylenediamine complex $[\text{Co}(\text{en})_3]^{3+}$ shows that the energy difference of the two extreme conformations is 1.8 Kcal/mole⁴³ and the crystal structure of $\Lambda\text{-}[\text{Co}(\text{en})_3]^{3+}$ confirmed the presence of the most stable conformation.⁴⁴

Experimental Section

A. Instrumentation

(i) Infrared Spectra (i.r.)

Solid state infrared spectra were obtained in KBr discs or nujol mulls in the range $(4000-250\text{ cm}^{-1})$ with a Perkin-Elmer 457 grating spectrometer. The low frequency region $450-200\text{ cm}^{-1}$ was recorded as nujol mulls between polythene or cesium iodide plates on a Perkin-Elmer 225 spectrometer. The infrared spectra obtained from Perkin-Elmer 457 spectrometer were calibrated by polystyrene film or water vapour from the machine. The low frequency region was also checked with the spectra obtained from Perkin-Elmer 225 spectrometer.

(ii) Raman Spectra (R)

The Raman spectra were recorded on solid samples using a Coderg CPH 100 Raman spectrometer equipped with a krypton laser source. The spectra were calibrated by plasma line. When a filter was used, the frequencies of the bands were marked directly from the dial reading of the instrument as the spectra were scanned.

(iii) Nuclear Magnetic Resonance Spectra (n.m.r.)

Nuclear magnetic resonance spectra were recorded in deuterated Chloroform, 1,1,2,2-tetrachloroethane, or d_6 -dimethylsulfoxide, with a Varian Model A-60 or a Varian Model HA-100 ^1H n.m.r. spectrometer. The Varian A-60 spectrometer was equipped with Varian variable temperature

units for the variable temperature studies. Tetramethylsilane (TMS) was used as an internal reference.

(iv) Ultraviolet and Visible Spectra (uv and visible)

The ultraviolet and visible spectra were recorded in water, methanol, chloroform or methylene chloride solution with a Unicam SP 800 spectrometer. The solid state nujol mull spectra of the copper(II) complexes were recorded on a Beckman DK2 spectrometer.

(v) Electron Spin Resonance Spectra (e.s.r.)

A JES-ME-3X spectrometer, operating at x-band frequency was used to record the electron spin resonance spectra at various temperatures.

(vi) Molecular Weight Measurements

Molecular weights were measured in 1,1,2,2-tetrachloroethane at 72°C using a Hewlett-Packard Vapour Pressure Osmometer, model 302B.

(vii) X-ray Powder Diffraction Pattern

X-ray powder diffraction patterns were measured using a Phillips Diffractometer using a Norelco x-ray generator with Cu-target. The diffraction patterns were recorded on chart using a PH 800 strip chart recorder.

(viii) Melting Point Apparatus

Melting points (uncorrected) were determined on a Fisher-John's melting point apparatus or Thomas Hoover Capillary melting point apparatus.

(ix) Conductivity Bridge

The conductivity in nitromethane was measured using an Impedance Comparator type 1605-AH conductivity bridge (General Radio Co.) at 25°C. The cell constant was determined by use of a standard aqueous solution of potassium chloride.

(x) Elemental Analyses

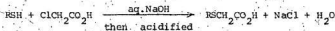
Microanalyses of carbon, hydrogen, sulfur, selenium and halogen were carried out by Alfred Bernhardt or Beller Microanalytical Laboratories, West Germany.

B. Preparation of Ligands(i) (Phenylthiadicetic Acid (Ph-SAH))

Commercial (phenylthiadicetic acid, which was purchased from Aldrich Chemical Co., was recrystallized from CHCl_3 /petroleum ether (30-60°C) before employing for reaction. m.p. 63.5 - 64°C.

(ii) o,m and p-Tolylthiadicetic Acids (o,m,p,-CH₃-SAH)

These ligands were prepared by treating the corresponding thiol with chloroacetic acid in aqueous sodium hydroxide.⁴⁶



The toluenethiols were purchased from Eastman Organic Chemicals.

The preparation of (o-tolylthio)acetic acid is given below. The meta- and para-derivatives were prepared similarly.

To $\text{o-CH}_3\text{C}_6\text{H}_4\text{SH}$ (50.0g, 0.410 mole) in 400 ml aqueous NaOH (32.8g, 0.820 mole) was added $\text{ClCH}_2\text{CO}_2\text{H}$ (38.7g, 0.410 mole) in 100 ml water. The mixture was refluxed for two hours, diluted to about 800 ml with water, and then acidified with 6.0 M HCl (0.820 mole, 137 ml). The white precipitate was filtered and repeatedly recrystallized from chloroform/petroleum ether (ca. 1:2 vol. ratio) to yield the required product, 61.2g (82.0%), m.p. 108.5-109.5°C. (lit. 107-8°C).⁴⁵

Yield of (m-tolylthio)acetic acid (88%), m.p. 66.8-67.5°C (lit. 67-68, ⁴⁷ 66.8-67.4°C⁴⁶). Yield of (p-tolylthio)acetic acid (68%), m.p. 93-94°C (lit. 88.5-90, ⁴⁷ 94.0-94.4°C⁴⁶).

(iii) (Phenylseleno)acetic Acid (Ph-SeAH) and (p-tolylseleno)acetic Acid (p-CH₃-SeAH)

The (phenylseleno) and (p-tolylseleno)acetic acids were prepared⁴⁸ by using Grignard reagent under inert atmosphere. Two methods of preparation of (p-tolylseleno)acetic acid are given below.

(p-Tolylseleno)acetic acid (p-CH₃-SeAH)

Method A:

p-Bromotoluene (100g, 0.585 mole) in 300 ml dry ether was added to magnesium metal (14.25g, 0.585 mole) and stirred for 10 hours. Selenium powder (46.2g, 0.585 mole) was added slowly to the above mixture and refluxed for 2 hours. The reaction solution was filtered and poured onto ice HCl mixture. The ether layer was quickly extracted with 97.5 ml of

6M NaOH. -To the aqueous solution of the extract was added 200 ml ethanol and 145 ml of 4M $\text{ClCH}_2\text{CO}_2\text{Na}$ solution. The solution was then concentrated and cooled to crystallize. The sodium salt obtained was recrystallized from H_2O -EtOH (8:2) until the yellow coloration of diselenide was absent. The free acid, obtained by treating the sodium salt with conc. HCl, was recrystallized from 10% ethanol. Yield: 26.8g (20%), m.p. 97-8°C (lit. 97-8°C).⁴⁹

Method B

The $\text{p-CH}_3\text{C}_6\text{H}_4\text{SeMgBr}$, prepared from the Grignard reagent, was hydrolyzed in ice HCl to convert to the yellow diselenide which was then reduced to form the p-tolylselenol.⁵⁰

To the diselenide (18.8g, 0.0549 mole) in 200 ml ether was added 20.0 ml conc. H_2SO_4 (diluted to 100 ml). Zinc dust was added slowly (ca. $3\frac{1}{2}$ hours) until all the yellow color vanished. The colorless ether layer was separated and extracted with 4M NaOH (~30 ml). To the aqueous extract was added 100 ml ethanol followed by 4M $\text{ClCH}_2\text{CO}_2\text{Na}$ (27.5 ml). The sodium salt of the product was recrystallized twice from H_2O -EtOH (8:2) and then acidified and recrystallized from water. The yield of sodium salt was 11.0g (79.7%).

(Phenylselenoacetic acid (Ph-SeAH))

(Phenylselenoacetic acid was prepared (by method A) by treating phenyl magnesium bromide with selenium powder, hydrolysing the product to give selenophenol, and condensing the selenophenol with chloroacetic acid.⁴⁸ to yield the required product (15%) m.p. 40°C (lit. 40°C).⁴⁸

C. Preparation of Platinum(II) and Palladium(II) Inner Complexes

(i) Bis(o-tolylthioacetato)platinum(II) $(\text{o-CH}_3\text{-S})_2\text{Pt}$

Several reactions at different temperatures have been carried out.

(1) Reaction at room temperature

An aqueous solution of (o-tolylthioacetic acid (0.7285g, 4.00 mmole) neutralized by potassium hydroxide in 74.0 ml water was added to an aqueous solution of potassium tetrachloroplatinate(II) (0.8304g, 2.00 mmole in 20.0 ml). The precipitate which formed after one hour at room temperature was filtered and washed with cold water and 95% ethanol. Further crops of the product could be obtained by concentrating the filtrate. Recrystallization of the product from water yielded pale-yellow crystals of the title compound; 0.9415g (92.5%), m.p. 214-215°C. Recrystallization from methanol or dichloroethane yielded an almost white powder of identical m.p. and infrared spectrum.

Anal. Calcd. for $\text{C}_{18}\text{H}_{18}\text{O}_4\text{S}_2\text{Pt}$:

C, 38.78 H, 3.25 S, 11.50

Found C, 38.83 H, 3.19 S, 11.32

(2) Reaction at elevated temperature

To a hot aqueous solution of potassium (o-tolyl-thioacetate (2.00 mmole in 100 ml water) was added an aqueous solution of potassium tetrachloroplatinate(II) (1.00 mmole in 30.0 ml water). The reaction mixture was heated on a steam bath. The fine yellow crystals which formed immediately were filtered while hot and the filtrate was cooled to room

temperature to yield a second crop; 0.4509g (80.8%), m.p. 215°C.

Infrared spectrum was identical to that of the recrystallized products in (1).

(3) Reaction at low temperature

To an aqueous solution of potassium(o-tolylthioacetate (2.00 mmole in 110 ml water) was added an aqueous solution of potassium tetrachloroplatinate(II) (1.00 mmole in 25.0 ml water). After stirring for about 70 minutes in an ice-bath, cloudiness of the solution was observed. The very pale-yellow powder was filtered after five hours and washed with cold water and dried to give the required product; 0.2617g (46.9%), m.p. 214.5°C.

Anal. Calcd. for $C_{18}H_{18}O_4S_2Pt$:

C, 38.78 H, 3.25 S, 11.50

Found: C, 38.96 H, 3.38 S, 11.33

(ii) Bis(p-tolylthioacetato)platinum(II) $(p-CH_3-SO_2)_2Pt$

Reactions at different metal-ligand ratios were investigated.

(i) Metal-ligand ratio (1:2)

An aqueous solution of potassium(p-tolylthioacetate (8.00 mmole in 140 ml water) was added to an aqueous solution of potassium tetrachloroplatinate(II) (1.660g, 4.00 mmole in 20.0 ml water). The pale-yellow precipitate which formed immediately was filtered after two hours at room temperature. A further crop was obtained by cooling the filtrate. Recrystallization of the product from hot water or methanol yielded pale yellow needle-shaped crystals of the required product;

2.001g (89.6%), m.p. 213.5-214°C.

Anal. Calcd. for $C_{18}H_{18}O_4S_2Pt$:

C, 38.78 H, 3.25 S, 11.50

Found C, 38.60 H, 3.37 S, 11.37

(2) Metal-ligand ratio (1:1)

An aqueous solution of potassium(p-tolylthioacetate (2.00 mmole in 30.0 ml water) was added to an aqueous solution of potassium tetrachloroplatinate(II) (2.10 mmole in 30.0 ml water). The pale yellow precipitate was filtered after ten minutes, washed and dried; 0.4674g (83.8%), m.p. 213°C. Infrared spectra and elemental analysis for platinum showed that a bis-complex was formed.

(3) Metal-ligand ratio (1:1) in the presence of bromide ion

An aqueous solution of potassium(p-tolylthioacetate (2.00 mmole in 10.0 ml water) was added slowly to an aqueous solution of potassium tetrachloroplatinate(II) (2.00 mmole) and potassium bromide (4.00 mmole in 30.0 ml water). A sticky precipitate formed in the reaction flask in about ten minutes. The precipitate was separated after half an hour and washed with water and acetone; 0.1788g (32%), m.p. 214-215°C. Again a bis-complex was formed.

Recrystallization of the products of reaction (1) or (2) from dichloroethane yielded a greenish yellow precipitate which contained solvent of crystallization m.p. 211°C. Drying of the recrystallized product in vacuo at -90°C overnight yielded the bis-complex m.p. 214°C.

Anal. Calcd. for $C_{18}H_{18}O_4S_2Pt$:

C, 38.78 H, 3.25 S, 11.50

Found C, 38.76 H, 3.37 S, 11.28

(iii) Bis(phenylthioacetato)platinum(II) (Ph-SA)₂Pt

To an aqueous solution of sodium(phenylthioacetate (0.7608g, 4.00 mmole in 30.0 ml water) was added an aqueous solution of potassium tetrachloroplatinate(II) (0.8304g, 2.00 mmole in 5.0 ml water). Reaction occurred immediately after mixing. The very pale yellow powder was filtered after stirring for an hour at room temperature, washed with water and alcohol and dried. Recrystallization by dissolving the compound at -50°C followed by slow evaporation of methanol at reduced pressure yielded pale yellow acicular crystals of the title compound; 0.8844g (63.6%), m.p. 216°C.

Anal. calcd. for C₁₆H₁₄O₄S₂Pt:

C, 36.29 H, 2.67 S, 12.11

Found C, 36.44 H, 2.80 S, 11.97

(iv) Bis(m-tolylthioacetato)platinum(II) (m-CH₃-SA)₂Pt

To an aqueous solution of potassium(m-tolylthioacetate (4.00 mmole in 44.0 ml water) was added an aqueous solution of potassium tetrachloroplatinate(II) (0.8302g, 2.00 mmole in 20.0 ml water). Reaction occurred rapidly. The very pale precipitate was filtered after stirring for half an hour. Recrystallization of the precipitate from absolute ethanol gave the title compound; 0.9934g (89.2%), m.p. 214°C.

Anal. calcd. for C₁₈H₁₈O₄S₂Pt:

C, 38.78 H, 3.25 S, 11.50

Found C, 38.71 H, 3.27 S, 11.37

(v) Bis(p-tolylselenoacetato)platinum(II) (p-CH₃-SeA)₂Pt

To an aqueous solution of sodium(p-tolylselenoacetate (0.004g, 4.00 mmole in 40.0 ml water) was added an aqueous solution of potassium tetrachloroplatinate(II) (0.8302g, 2.00 mmole in 20.0 ml water). The precipitate was filtered after stirring for two hours and washed with cold water. Recrystallization from water/methanol yielded shining yellow acicular crystals of the title compound; 1.075g (82.5%), m.p. 210°C.

Anal. calcd. for C₁₈H₁₈O₄Se₂Pt:

| | | | |
|-------|----------|---------|----------|
| | C, 33.19 | H, 2.78 | Se, 24.2 |
| Found | C, 33.14 | H, 2.87 | Se, 24.1 |

Recrystallization of the compound from dichloroethane yielded a very pale-yellow powder which had the same infrared spectrum and melting point as the above.

(vi) Bis(phenylselenoacetato)platinum(II) (Ph-SeA)₂Pt

An aqueous solution of sodium phenylselenoacetate (0.4729g, 2.00 mmole in 20.0 ml water) was added to an aqueous solution of potassium tetrachloroplatinate(II) (0.4151g, 1.00 mmole in 10.0 ml water). Reaction occurred immediately. The very pale-yellow precipitate was filtered after one hour at room temperature. Recrystallization from boiling water or 1:1 methanol-water yielded glittering pale yellow needle-shaped crystals. Recrystallization from dichloroethane yielded a pale-yellow powder of the title compound; 0.5338g (94%), m.p. 221-222°C.

Anal. calcd. for $C_{16}H_{14}O_4SePt$:

C, 30.84 H, 2.26 Se, 25.3

Found C, 30.78 H, 2.11 Se, 25.5.

(vii). Bis(o-tolylthioacetato)palladium(II) $(o-CH_3-SA)_2Pd$

An aqueous solution of potassium(o-tolylthioacetate (4.00 mmole in 30.0 ml water) was added slowly to an aqueous solution of potassium tetrachloropalladate(II) (0.6528g, 2.00 mmole in 25.0 ml water). The deep yellow precipitate was filtered after four and three quarters hours. Recrystallization from dichloromethane yielded fine fibrous crystals of the required compound; 0.853g (91%), m.p. 158°C.

Anal. calcd. for $C_{18}H_{18}O_4S_2Pd$:

C, 46.13 H, 3.87 S, 13.68

Found C, 46.21 H, 3.96 S, 13.62

Recrystallization of the compound from chloroform yielded orange-yellow fine needle-shaped crystals which contained chloroform of crystallization. The solvent of crystallization was not completely removed after heating at 70°C in vacuo overnight. m.p. 159°C.

Anal. calcd. for $C_{18}H_{18}O_4S_2Pd \cdot 1/5CHCl_3$:

C, 43.55 H, 3.65 S, 12.71

Found C, 43.26 H, 3.57 S, 12.81

Mass spectrum also indicated the presence of chloroform of crystallization. Removal of the solvent at higher temperature caused partial decomposition. The color of the compound changed from orange-yellow to brownish color and the m.p. dropped to 154°C.

(vifi) Bis(phenylthioacetato)palladium(II) (Ph-SA)₂Pd

To an aqueous solution of sodium(phenylthioacetate) (0.7608g, 4.00 mmole in 35.0 ml water) was added an aqueous solution of potassium tetrachloropalladate(II) (0.6528g, 2.00 mmole in 15.0 ml water). Reaction occurred immediately. The yellow precipitate was filtered after stirring for half an hour, washed with cold water and dried in vacuo over P_2O_5 to give the hydrated compound; 0.7822g (85.3%), m.p. 143°C (compound A). Dehydration of compound A at -100°C in vacuo corresponded to the loss of half a molecule of water to give the anhydrous compound B; m.p. 159°C.

Anal. calcd. for $C_{16}H_{14}O_4S_2Pd$ (product of (A) after dehydration);

C, 43.59 H, 3.20 S, 14.55

Found C, 43.40 H, 3.30 S, 14.42

The hydrated compound was dissolved in 80% methanol below 40°C. Evaporation of methanol under reduced pressure was carried out with slow flow of nitrogen. Orange acicular crystals separated out from the solution. m.p. 160°C.

Anal. calcd. for $C_{16}H_{14}O_4S_2Pd$ (B)

C, 43.59 H, 3.20 S, 14.55 Pd, 24.14

Found C, 43.54 H, 3.32 S, 14.33 Pd, 24.32

The filtrate of (B) was quickly dried by pumping off the solvent. The yellow residue showed identical infrared spectrum to compound A before dehydration. However, heating compound A above 60°C in methanol resulted in decomposition to a brownish powder.

Recrystallization of compound A from dichloroethane yielded an orange-yellow powder whose infrared spectrum is identical to B. The

dichloroethane solution of A was also partially decomposed to give a brownish-red powder after keeping it in the refrigerator for about one month.

Compound A is fairly soluble in acetone. However, the ^1H n.m.r. spectrum in acetone showed the absence of signals for the complex.

(ix) Dichloro-bis(phenylthioacetic acid)palladium(II) $(\text{Ph-SAH})_2\text{PdCl}_2$

The hydrated compound $(\text{Ph-SAH})_2\text{Pd}\cdot\text{H}_2\text{O}$ (0.9120g, 2.00 mmole) was treated with 3M HCl and the residue was recrystallized from 95% ethanol-2N HCl to give the dichloro-complex; 0.6640g (64.7%) m.p. 157°C.

Anal. calcd. for $\text{C}_{16}\text{H}_{16}\text{O}_4\text{Cl}_2\text{S}_2\text{Pd}$:

C, 37.41 H, 3.14 S, 12.48

Found: C, 37.30 H, 3.23 S, 11.59

(x) Bis(m-tolylthioacetato)palladium(II) $(\text{m-CH}_3\text{SA})_2\text{Pd}$

An aqueous solution of potassium(m-tolylthioacetate) (4.00 mmole in 30.0 ml water) was added to an aqueous solution of potassium tetrachloropalladate(II) (0.6528g, 2.00 mmole in 25.0 ml water). Reaction occurred immediately. The yellow precipitate was filtered after stirring for one hour at room temperature. Recrystallization from water and drying in vacuo over P_2O_5 gave the required hydrated compound; 0.7840g (82.0%) m.p. 155-156°C.

Anal. calcd. for $\text{C}_{18}\text{H}_{18}\text{O}_4\text{S}_2\text{Pd}\cdot\frac{1}{2}\text{H}_2\text{O}$: (A)

C, 45.24 H, 4.01 S, 13.42

Found: C, 45.10 H, 3.84 S, 13.61

Recrystallization of the hydrated compound from CH_2Cl_2 yielded

the anhydrous compound as a yellow powder; m.p. 160-161°C.

Anal. calcd. for $C_{18}H_{18}O_4S_2Pd$: (B)

C, 46.13 H, 3.87 S, 13.68

Found C, 46.26 H, 3.85 S, 13.52

Recrystallization of A from chloroform also gave compound B.

Infrared spectra of A and B are different.

(xi) Bis(p-tolylthioacetato)palladium(II) (p-CH₃-SA)₂Pd

An aqueous solution of potassium(p-tolylthioacetate) (4.00 mmole in 35.0 ml water) was added slowly to an aqueous solution of potassium tetrachloropalladate(II) (0.6528g, 2.00 mmole in 15.0 ml water). The orange-yellow precipitate was filtered after half an hour, washed with cold water and dried over P₂O₅. m.p. 149°C (compound A). Dehydration of the compound at -95°C in vacuo gave the title compound; 0.8163g (87%).

Anal. calcd. for $C_{18}H_{18}O_4S_2Pd$ (product of A after dehydration):

C, 46.13 H, 3.87 S, 13.68

Found C, 46.27 H, 3.94 S, 13.57

Recrystallization of compound A from chloroform yielded the anhydrous compound. m.p. 175°C.

Anal. calcd. for $C_{18}H_{18}O_4S_2Pd$: (B)

C, 46.13 H, 3.87 S, 13.68

Found C, 46.09 H, 3.89 S, 13.52

Recrystallization of A from CH₂Cl₂, CH₃OH, (CH₃)₂CO or CH₂Cl₂-C₆H₆ mixed solvents all yielded compound B. Yet the infrared spectra and m.p. varied slightly, probably because the isomer ratio changed slightly.

(xii) Bis(p-tolylselenoacetato)palladium(II): (p-CH₃-SeA)₂Pd

An aqueous solution of sodium(p-tolylselenoacetate (1.004g, 4.00 mmole in 40.0 ml water) was added to an aqueous solution of potassium tetrachloropalladate(II) (0.6528g, 2.00 mmole in 25.0 ml water). Reaction occurred immediately. The yellow precipitate was filtered after half an hour, washed with cold water and dried over P₂O₅ in vacuo. Water of crystallization could not be removed after drying in vacuo at -88°C for eight hours; 0.9387g (80.8%), m.p. 140°C (dehydrated), 147°C (decomposed).

| | |
|--|-----|
| Anal. calcd. for C ₁₈ H _{18.4} O ₄ Se ₂ Pd.H ₂ O: | (A) |
| C, 36.54 H, 3.48 Se, 26.71 | |
| Found C, 37.05 H, 3.48 Se, 26.90 | |

Recrystallization of A from CH₂Cl₂ yielded fibrous crystals, m.p. 157°C. It could be recrystallized from chloroform or acetone, but it decomposed in acetone at high temperature or in acetone at 0°C for five days. Infrared spectroscopy showed that the sample recrystallized from various solvents yielded identical spectra.

Elemental analysis of the sample recrystallized from dichloromethane corresponded to the anhydrous form.

| | |
|---|-----|
| Anal. calcd. for C ₁₈ H ₁₈ O ₄ Se ₂ Pd: | (B) |
| C, 38.43 H, 3.22 Se, 28.06 | |
| Found C, 38.49 H, 3.19 Se, 27.98 | |

(xiii) Bis(phenylselenoacetato)palladium(II): (Ph-SeA)₂Pd

An aqueous solution of sodium(phenylselenoacetate (0.944g, 4.00

mmole in 40.0 ml water) was added slowly to an aqueous solution of potassium tetrachloropalladate (II) (0.6528g, 2.00 mmole in 25.0 ml water). The reaction mixture was stirred at room temperature for one hour. The yellow precipitate was filtered, washed with cold water and dried in vacuo over P_2O_5 . Recrystallization of the product from dichloromethane gave the required anhydrous product as a bright yellow fibrous crystals; 0.7925g (81.5%), m.p. 153-154°C.

Anal. calcd. for $C_{16}H_{14}O_4Se_2Pd$: (B)

C, 35.95 H, 2.64 Se, 29.5

Found C, 36.03 H, 2.65 Se, 29.3

Recrystallization from dichloroethane yielded a greenish yellow fibrous crystals and from chloroform/carbon tetrachloride yielded a glittering orange-yellow powder. Dissolution of the compound in 1:1 ethanol-water (without heating) followed by evaporation of the alcohol in vacuo yielded brownish yellow glittering sheets. All samples have infrared spectra similar to that of the sample recrystallized from dichloromethane. However, the aqueous solution of the compound decomposed after it was kept for about a month at 0°C. On heating, the alcoholic solution of the compound yielded a brownish-yellow fibre-like residue, m.p. 192-194°C. The infrared spectrum showed the presence of free carboxylate group and the 60-MHz 1H n.m.r. spectrum in d_6 -DMSO showed the deshielded phenyl ring protons and a broad singlet at 5.85 τ , but no acidic proton could be detected.

Results and Discussion

Arylthio- or arylseleno-acetic acids may behave as uni- or bidentate ligands when they coordinate to metal ions. The reactions of the ligands $\text{RC}_6\text{H}_4\text{XCH}_2\text{CO}_2^-$ (where $\text{X}=\text{S}$, $\text{R}=\text{H}$, $\text{o}-\text{CH}_3$, $\text{m}-\text{CH}_3$, $\text{p}-\text{CH}_3$; and $\text{X}=\text{Se}$, $\text{R}=\text{H}$, $\text{p}-\text{CH}_3$) with PtCl_4^{2-} or PdCl_4^{2-} formed the inner complexes, ML_2 . Unlike α -amino acids or the corresponding arylsulfoxyacetate, for which complexes with a 1:1 metal-ligand ratio could be isolated easily, these sulfur and selenium ligands formed only 1:2 complexes even when a metal-ligand ratio of 1:1 was used. This suggests that the 1:2 complexes are very much more stable than the 1:1 complexes.

Recently, the mechanism of the substitution reaction of dichloro-(methionine)platinum(II) with L-methionine has been investigated. A kinetic study under pseudo-first order conditions in aqueous solution showed that this reaction took place in two consecutive steps. The first step involved the replacement of one chloride ion by the sulfur atom of the entering amino acid. The rate of the first, which was a slow one, depended on the concentration of the entering amino acid and on the concentration of chloride ion. The second step involved closure of the methionine ring and the rate was a linear function with respect to the reciprocal of the hydrogen ion concentration.⁵¹

The reactions investigated here proceeded very fast. Qualitative comparison of the rate of reaction showed that the sulfur- or selenium-containing ligands reacted much faster than the corresponding amino acid. The faster rate of reaction may be related to the higher trans effect of sulfur and selenium relative to nitrogen in these systems.⁵²

The dichloro(L-methionine)platinum(II) was prepared by the re-

action of potassium tetrachloroplatinate(II) with L-methionine in aqueous solution.⁵³ The bis(L-methionine)platinum(II) dichloride dihydrate $[\text{Pt}(\text{S-N})_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ was prepared by the reaction of $[\text{Pt}(\text{S-N})\text{Cl}_2]$ with an equimolar amount of L-methionine in aqueous solution.⁵⁴

Thus, it is reasonable to assume that in the present system the first ligand is attached to Pt(II) or Pd(II) through the sulfur or selenium atom (and not through the acetate group), probably followed by ring closure. When the second molecule of ligand is introduced, the sulfur or selenium atom of the ligand should take the place of the Cl atom in the trans position with respect to the sulfur or selenium atom of the cyclically attached ligand molecule; subsequent ring closure should give the trans isomer.

A. Structural Consideration of the Complexes

The structural elucidation is based mainly on the elemental analyses, spectroscopic data such as infrared, Raman, proton magnetic resonance, electronic spectra and others which are available.

The conductivity measurements of the platinum complexes in nitromethane and the palladium complexes in chloroform show that they are non-electrolytes. Elemental analyses are consistent with the empirical representation $\text{ML}_2 \cdot x\text{H}_2\text{O}$ (where $\text{M}=\text{Pt(II), Pd(II)}$, $\text{L}=\text{arylthio-}$ or $\text{arylseleno-acetate}$, $x=0, 1/2, 1$) and molecular weight data in 1,1,2,2-tetrachloroethane confirm their mononuclear character in solution (Table 5). The sharp ^1H n.m.r. spectra for these complexes are consistent with diamagnetic species indicating little departure from planar structures, so that an assumption of square planar geometries seems appro-

Table 5

Molecular Weight of Bis-complexes^a

| Compound ^b | Calcd. | Found |
|--|--------|-------|
| (Ph-SA) ₂ Pd ^c | 440.8 | 481 |
| (Ph-SA) ₂ Pd ^d | 440.8 | 465 |
| (o-CH ₃ -SA) ₂ Pd | 468.9 | 487 |
| (m-CH ₃ -SA) ₂ Pd | 468.9 | 493 |
| (p-CH ₃ -SA) ₂ Pd | 468.9 | 474 |
| (Ph-SeA) ₂ Pd | 534.6 | 545 |
| (p-CH ₃ -SeA) ₂ Pd | 562.7 | 573 |
| (o-CH ₃ -SA) ₂ Pt | 557.6 | 549 |
| (m-CH ₃ -SA) ₂ Pt | 557.6 | 596 |
| (p-CH ₃ -SA) ₂ Pt | 557.6 | 520 |
| (p-CH ₃ -SeA) ₂ Pt | 651.4 | 694 |
| (Ph-SA) ₂ Pt | 529.5 | 555 |
| (Ph-SeA) ₂ Pt | 623.3 | e |

a In 1,1,2,2-tetrachloroethane at -72°C.

b Abbreviations: Ph-SA = PhSCH₂CO₂⁻, Ph-SeA = PhSeCH₂CO₂⁻,
o,m,p-CH₃-SA = o,m,p-CH₃C₆H₄SC₂CO₂⁻ and
p-CH₃-SeA = p-CH₃C₆H₄SeCH₂CO₂⁻.

c Product obtained from dehydration of the hydrated compound
in vacuo.

d Product recrystallized from dichloroethane.

e Insoluble.

prate.

The unsymmetrical nature of the bidentate ligand $\text{RC}_6\text{H}_4\text{XCH}_2\text{CO}_2^-$ ($\text{X}=\text{S}, \text{Se}$) could lead to geometric isomerism among its metal chelates. Cis and trans isomers might be expected with the square planar Pt(II) and Pd(II) derivatives. The dipole moment of a cis complex is higher than that of the trans complex which has a moment close to zero. However, the bis-compounds prepared in the present work are insoluble in symmetrical organic solvents such as carbon tetrachloride, cyclohexane, benzene and others. Hence, useful dipole moment measurements could not be carried out.

X-ray crystallographic studies of chelated complexes of sulfur- and selenium-containing ligands, for example, dichloro(1,2-diisopropylselenoethane)palladium(II)⁵⁵ and dichloro(L-methionine)platinum(II)⁵⁶ have indicated that the chalcogen atoms are pyramidal in the ground state, with the fourth position about these atoms presumably occupied by a lone pair of electrons. Thus, the chalcogen atoms are centers of asymmetry. Similarly the chelated complexes $\text{M}(\text{RC}_6\text{H}_4\text{XCH}_2\text{CO}_2)_2$ ($\text{X}=\text{S}, \text{Se}$, $\text{M}=\text{Pt(II)}, \text{Pd(II)}$) studied here have dissymmetry imposed not only by the conformation of chelated rings but also by the asymmetry of the ligand atoms.

In principle, interconversion of conformers of five-membered rings can take place by ring inversion (i.e. interchange of envelope and half-chair conformations). The phenyl substituents on the pyramidal sulfur atoms of the bis-complexes may possess pseudo axial or equatorial character with respect to the chelated rings. In addition, they may be projected on the same side (syn) or on different sides (anti) of the

chelated rings.

Conformational studies of amino acid complexes have suggested that non-planar, puckered or enveloped forms are preferable for the five-membered chelated rings, but that the rings are less puckered than those of similar diamines.^{57,58,59} Some possible conformations of the chelated rings of the inner complexes are shown in Fig. 2. For simplicity, only one chelated ring and one enantiomeric form are shown.

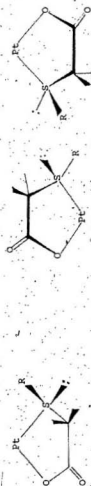
An x-ray crystallographic study of dichloro(S-methyl-L-cysteine)-palladium(II) monohydrate has shown that there are two crystallographically independent molecules with the same square planar coordination involving S and N from the amino acid ligand and two Cl atoms. The coordinated five-membered ring has λ conformation.⁶⁰ Thus, the five-membered chelated rings of the Pt(II) and Pd(II) complexes studied here may possibly have similar conformations.

B. Vibrational Spectra

The infrared and Raman spectra of the platinum complexes were obtained in the solid state. Only the infrared spectra of the palladium complexes were obtained as these palladium complexes were easily decomposed in the laser light of the Raman spectrometer.

(a) Higher Frequency Region

The vibrational spectra in this region provide the information of how the carboxylates are coordinated to the metal ions. The carboxylate group may coordinate to a metal ion either as a

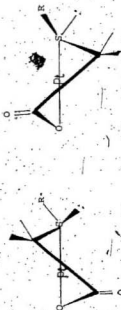


eclipsed

IX

puckered

X



enveloped

XI

Fig. 2 Some possible conformations of the five membered chelated rings.

bidentate ligand, to give a symmetrically bridged structure, or as a unidentate ligand in a mononuclear molecule. These two cases can be differentiated by infrared spectroscopy. For the carboxylate as a unidentate ligand (XII), a wide separation of $\nu_a(\text{CO}_2)$ and $\nu_s(\text{CO}_2)$ compared with the free ion is expected because of a decrease in the equivalence of the C-O bonds. For the symmetrically bridged structure (XIII), both the $\nu_a(\text{CO}_2)$ and $\nu_s(\text{CO}_2)$ frequencies are shifted in the same direction upon changing to metal. Furthermore, for structure (XIII), the separation values $\Delta\nu(\text{CO}_2)$ are comparable to those of the free ion, e.g. sodium or potassium salt of the parent acid, while the separation value $\Delta\nu(\text{CO}_2)$ for unidentate carboxylate complex (XII) is usually much larger.⁶¹



XII



XIII

For these bis- complexes studied here, the coordination of the carboxylate group shifts the $\nu_a(\text{CO}_2)$ to higher frequency and $\nu_s(\text{CO}_2)$ to lower frequency compared with its free ion. The $\nu_a(\text{CO}_2)$ and $\nu_s(\text{CO}_2)$ of the free ion, for example, $\text{o-CH}_3\text{C}_6\text{H}_4\text{SCH}_2\text{CO}_2\text{K}^+$, are at about 1580 and 1385 cm^{-1} respectively. The $\nu_a(\text{CO}_2)$ and $\nu_s(\text{CO}_2)$ are at ~1650 and ~1285 cm^{-1} respectively for the corresponding platinum complex and at 1640 and 1297 cm^{-1} respectively for the palladium complex. The wide separation of the antisymmetric and symmetric carboxyl stretching frequencies $\Delta\nu(\text{CO}_2)$ of these complexes indicates that the carboxylate group acts as a unidentate ligand in these compounds. (see Table 6).

Table 6
Infrared and Raman Data of Bis-complexes

| | | Frequency cm^{-1} | | | |
|-----------------------------------|------|----------------------------|-----------------------|-------------------------|---|
| Compound | | $\nu_a(\text{COO})$ | $\nu_s(\text{COO})$ | $\Delta\nu(\text{COO})$ | $\nu_{\text{C-S}}$ or $\nu_{\text{C-Se}}$ |
| (Ph-SA) $_2$ Pt | i.r. | 1650(s) | 1290(s) | 360 | 731(sh) |
| | R | 1654(mw) | 1279(mw) | 375 | 731(n) |
| (Ph-SeA) $_2$ Pt | i.r. | 1655(s) | 1275(s) | 380 | 666(sh) |
| | R | 1674(mw) | 1279(mw) | 395 | 666(n) |
| (o-CH $_3$ -SA) $_2$ Pt | i.r. | 1650(s) | 1297(s) | 353 | 730(mw) |
| | R | 1654(mw) | 1287(mw) | 367 | 731(n) |
| (m-CH $_3$ -SA) $_2$ Pt | i.r. | 1650(s) | 1279(s) | 372 | 730(n) |
| | R | 1662(mw) | 1284(mw) | 378 | 733(n) |
| (p-CH $_3$ -SA) $_2$ Pt | i.r. | 1655(s) | 1280(s) | 375 | 730(m) |
| | R | 1668(mw) ^a | 1306(mw) ^a | 362 | 729(mw) |
| | | 1646(mw) | 1286(mw) | | |
| (p-CH $_3$ -SeA) $_2$ Pt | i.r. | 1635(s) | 1285(s) | 350 | — |
| (p-CH $_3$ -SeA) $_2$ Pt.H $_2$ O | i.r. | 1655(s) | 1300(s) ^a | 366 | 665(sh) |
| | | — | 1278(s) | | |
| | R | 1659(mw) | 1312(mw) | 364.5 | 635(n) |
| (Ph-SA) $_2$ Pd | i.r. | 1670(s) ^a | 1313(s) ^a | 351.5 | 722(n) |
| | | 1620(s) | 1274(s) | | |
| | R | 1655(w) ^a | 1320(w) | — | 723(mw) |
| | | 1620(w) | 1275(w) | | |
| (Ph-SA) $_2$ Pd.3/2H $_2$ O | i.r. | 1640(s) ^a | 1280(s) | 360 | 726(mw) |
| (o-CH $_3$ -SA) $_2$ Pd | i.r. | 1640(s) | 1297(s) | 343 | 718(mw) |
| (m-CH $_3$ -SA) $_2$ Pd | i.r. | 1640(s) | 1280(s) | 360 | 685(n) |
| (p-CH $_3$ -SA) $_2$ Pd | i.r. | 1640(s) | 1310(s) ^a | 346.5 | 700(mw) |
| | | — | 1277(s) | | |
| | R | 1641(w) | 1307(w) | 334 | 710(mw) |
| (p-CH $_3$ -SA) $_2$ Pd.H $_2$ O | i.r. | 1640(s) | 1300(s) | 340 | 719(n) |
| (p-CH $_3$ -SeA) $_2$ Pd | i.r. | 1620(s) | 1285(s) | 335 | 676(w) |
| (p-CH $_3$ -SeA) $_2$ Pd.H $_2$ O | i.r. | 1620(s) | 1292(s) | 328 | 661(w) |
| | i.r. | 1646(s) | 1266(s) | 375 | 676(w) |

a. Two equally strong bands are observed.

The antisymmetric and symmetric carboxyl stretching frequencies of all the other complexes are similarly assigned and their corresponding $\nu_a(\text{CO}_2)$ and $\nu_s(\text{CO}_2)$ stretching frequencies are located in Table 6.

It has been found in the amino acid chelates that the magnitude of the band shifts of the carboxyl stretching frequency increased as the metal changed in the order $\text{Ni(II)} < \text{Cu(II)} < \text{Pd(II)} < \text{Pt(II)}$ and that the strength of the metal-oxygen coordinate bond became stronger in the same order of metals.⁶²

The slightly larger difference in antisymmetric and symmetric stretching frequencies, $\Delta\nu(\text{CO}_2)$, for the platinum complex than for the corresponding palladium complex indicates that the platinum-oxygen bond is probably slightly stronger than the corresponding palladium-oxygen bond.

(i) Platinum Complexes

The infrared and Raman spectra of the platinum complexes, which were obtained in the solid state, are shown in Figs. 3-7 for the region below 1800 cm^{-1} .

In the case of the selenium complexes $(p\text{-CH}_3\text{-SeA})_2\text{Pt}$, $(\text{Ph-SeA})_2\text{Pt}$, the recrystallized product from water or methanol/water resulted in glittering crystals which contain one molecule of water of crystallization. Comparisons of the infrared spectra of the hydrated and anhydrous form (dehydrated by recrystallization from dichloroethane) show that they are similar, with the hydrated form exhibiting the water bands at 3500 and 3400 cm^{-1} due to $\nu_a(\text{H}_2\text{O})$ and $\nu_s(\text{H}_2\text{O})$ respectively and at 1605 cm^{-1} due to $\delta(\text{H}_2\text{O})$. The bands in the hydrated form are broader. The water

molecule in the hydrated form may be lattice water or coordinated water. Both types of water exhibit modes below 800 cm^{-1} .⁶³ Typical lattice type water, according to van der Elst and Robinson,⁶⁴ shows two absorptions in the region $700\text{--}335\text{ cm}^{-1}$. In the case of coordinated water, translational and rotational degrees of freedom are replaced by the vibration $\nu(\text{M-OH}_2)$, twist and rock. X-ray analysis on bis(glycinato)-cadmium(II) monohydrate has indicated that two glycinate molecules coordinated to the metal atom by forming a trans planar structure, while the other two positions of octahedron were occupied by carboxyl oxygens of neighboring ligands. The oxygens of the carboxyl group were hydrogen bonded to a water molecule of the hydrated crystal.⁶⁵ Since the platinum(II) complexes of the present study may be square planar in structure, it is probable that the water molecules in these complexes are lattice-type water.

The assignment of trans structure based on infrared and Raman spectra may be compared with the recent studies of bis- β -mercaptoethylamine complexes. The vibrational spectra of the monomeric bis- β -mercaptoethylamine complexes of Ni(II), Pd(II) and Pt(II) have been reexamined.⁶⁶ Using the evidence of both the infrared and Raman spectra, a trans square planar structure was suggested. In an earlier study, the same Pd(II) and Ni(II) compounds were assigned to a cis structure based on the number of metal ligand stretching modes assigned in the infrared spectra of the complexes by use of the isotopic substitution of the metal atom and the deuteration shifts of the ligand.⁶⁷ An x-ray crystallographic study has shown a similar monomeric Ni(II) complex of N, N'-dimethyl- β -mercaptoethylamine to be trans square planar in the solid state.⁶⁸

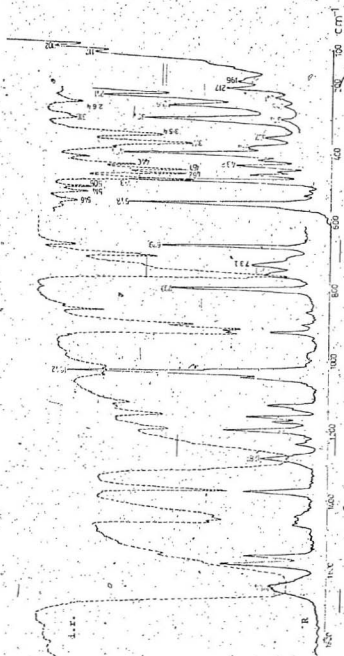


Fig. 3 Infrared and Raman Spectra of $(o\text{-Cl}_{13}\text{-SA})_2\text{Pt}$.

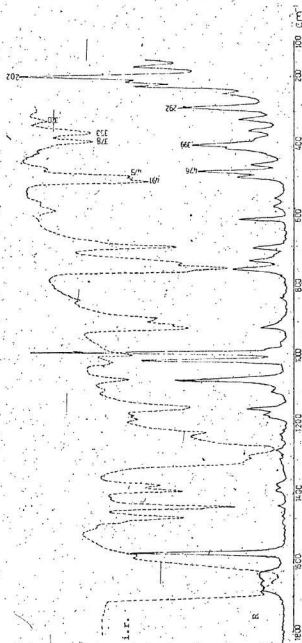


Fig. 4 Infrared and Raman Spectra of $(\text{Ph-SA})_2\text{Pt}$.

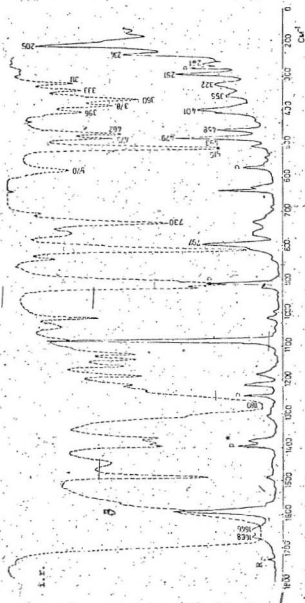


Fig. 5 Infrared and Raman spectra of (p-CH₃-SA)₂Pt.
(P = plasma line)

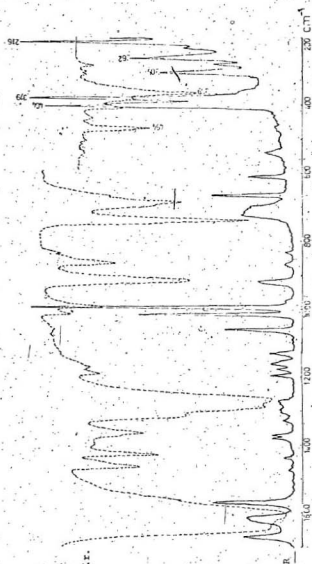


Fig. 6 Infrared and Raman spectra of (Ph-Se)₂Pt.

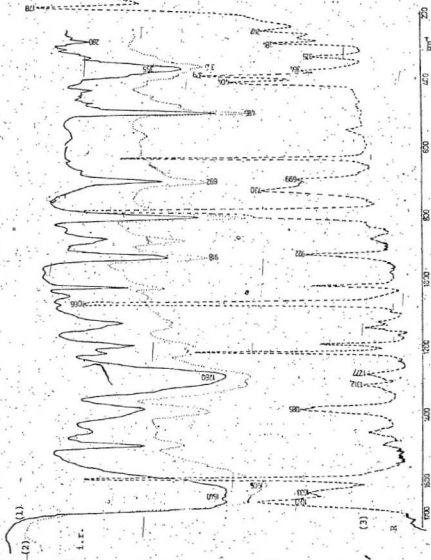


Fig. 7. Infrared spectra of (1) $(p\text{-CH}_3\text{-SeA})_2\text{Pt}$, (2) $(p\text{-CH}_3\text{-SeA})_2\text{Pt}\cdot\text{H}_2\text{O}$ and Raman spectrum of (3) $(p\text{-CH}_3\text{-SeA})_2\text{Pt}\cdot\text{H}_2\text{O}$.

(ii) Palladium Complexes

The initial palladium complexes and the product recrystallized from water contain water of crystallization. Recrystallization of the product from organic solvents yielded the anhydrous form. The properties of the two forms in the solid state are different (x-ray diffraction pattern, m.p. and i.r.). However, their solution properties (^1H n.m.r., electronic spectra) are similar. The infrared spectra of the two forms of the palladium complexes in the solid state are shown in Figs. 8-10.

The $\Delta\nu(\text{CO}_2)$ separation is larger in the anhydrous form than the hydrated form. The infrared spectra below 600 cm^{-1} show a marked difference between the two forms in the low frequency region.

Because of the low stability of the palladium complexes towards laser light, only the Raman spectra of anhydrous $(\text{p-CH}_3\text{-SA})_2\text{Pd}$ and $(\text{Ph-Sa})_2\text{Pd}$ were obtained. The infrared spectra of the hydrated compounds generally exhibit fewer but broader bands than those of the anhydrous forms.

Although cis-trans isomerism of the hydrated and anhydrous form is possible, dialkylsulfides⁶⁹ and dialkyl- and diaryl-selenides⁷⁰ form monomeric Pd(II) complexes $(\text{Pd}(\text{R}_2\text{E})_2\text{X}_2)$, (where $\text{E}=\text{S}$ and Se , $\text{X}=\text{halides}$), which only exist in the trans configuration, as confirmed by x-ray diffraction of trans- $\text{Pd}(\text{Et}_2\text{Se})_2\text{Cl}_2$.⁷¹

The infrared spectrum of the product recrystallized from water was unchanged from that of the original reaction product. However, dehydration did cause shifts in the spectra. Various solvents, such as methanol, chloroform, dichloromethane and acetone, had the same effect even when the conditions were extremely mild.

It is known that the infrared frequencies of a compound differ from one state to another. The shifts of the infrared spectra from the hydrated state to the anhydrous state may be as much as 30 cm^{-1} .⁷² The presence of water of crystallization may favour a certain conformation. Whether the shifts of the band in the hydrated complex studied here simply result from a difference of state or a difference in their conformations is not clear.

Fig. 10a shows the infrared spectra ($1800\text{--}250 \text{ cm}^{-1}$) of $(\text{Ph-Sa})_2\text{Pd}$ and $(\text{Ph-Sa})_2\text{Pd}\cdot\text{H}_2\text{O}$. The spectra of the anhydrous form isolated from methanol and dichloroethane are identical, however, they are more complicated than those of the hydrated form obtained from the initial product or recrystallized from water. The anhydrous form seems to have lower symmetry than that of the hydrated form (see also Figs. 8, 9 and 10).

Coordination of water to Pd(II) is not common because the "soft" metal ion Pd(II) forms only a weak bond with "hard" oxygen. The hydrated state of these palladium complexes probably involves hydrogen bonding of water and the carboxyl groups. Thus, the shifts of $\nu_a(\text{CO}_2)$ to lower frequency and $\nu_s(\text{CO}_2)$ to higher (a decrease of $\Delta\nu(\text{CO}_2)$) frequency in the hydrated form seem to agree with the hydrogen bonding at the carboxyl group.

When the hydrated $(\text{Ph-Sa})_2\text{Pd}\cdot\text{H}_2\text{O}$ was treated with 3M HCl , the complex $\text{Pd}(\text{Ph-SaH})_2\text{Cl}_2$ was isolated. The infrared spectrum of this compound shows a broad band at $\sim 3000 \text{ cm}^{-1}$ due to the O-H stretching frequency of the free carboxylic acid and three strong bands at 1700 , 1395 and 1265 cm^{-1} corresponding to the carboxyl stretching frequencies in the free acid. In the low frequency region, a moderately strong band at 342 cm^{-1}

* For the Figures 10a-10g see the Appendix.

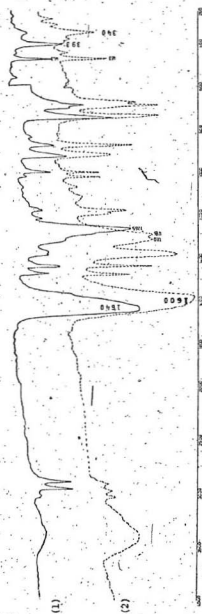


Fig.-8 Infrared spectra of (Ph-SeA)₂Pd (1) and (Ph-SeA)₂Pd.H₂O (2).

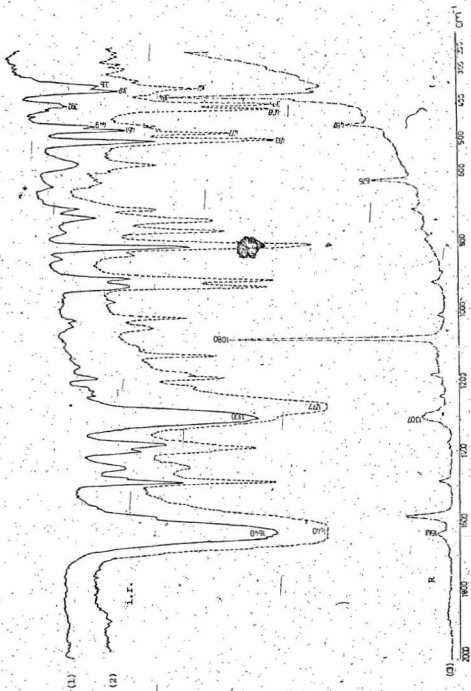


Fig. 9 Infrared spectra of $(p\text{-CH}_3\text{-SA})_2\text{Pd.H}_2\text{O}$ (1), $(p\text{-CH}_3\text{-SA})_2\text{Pd}$ (2), and Raman spectrum of $(p\text{-CH}_3\text{-SA})_2\text{Pd}$ (3).

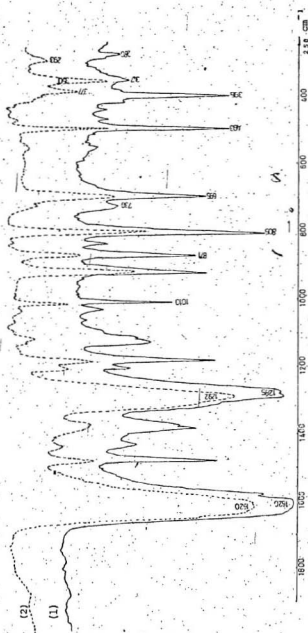
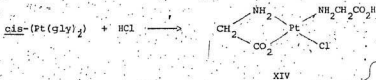


Fig. 10. Infrared spectra of (p-CH₃-SeA)₂Pd (1) and (p-CH₃-SeA)₂Pd.H₂O (2).

is assigned to Pd-Cl stretching frequency. Fergusson et al. assigned $\nu_{\text{Pd-Cl}}$ of the trans-Pd(R₂S)₂Cl₂ at 330-362 cm⁻¹.¹⁵³ The presence of only one Pd-Cl stretching frequency suggests that the compound is probably trans in structure, bonded through the thio groups of the ligands and two chlorine atoms.

The formation of a trans complex suggests that the original hydrated form is probably trans in structure. It has been shown that the reactions of cis- and trans-bis(glycinato)platinum(II) with concentrated hydrochloric acid were different, the trans isomer giving trans-dichlorobis-(glycine)platinum(II) in which the glycine ligands were bound to the metal through their nitrogen atoms only, whereas the cis isomer only reacted with one mole of hydrochloric acid to give (Pt(gly)(gly H)Cl) (where gly=NH₂CH₂CO₂⁻, and gly H=NH₂CH₂CO₂H).⁷³



Bellamy⁷⁴ and Sheppard⁷⁵ show that the frequency for the C-S bond decreases according to the following sequence:

Sulfur attached to an aromatic ring > thiols > sulfides > disulfides

The C-S stretching in methyltolylsulfides, sulfoxides and sulfones are found to be at 722, 680, 760 cm⁻¹ respectively.⁷⁶ The assignments of $\nu_{\text{C-S}}$ at 730 cm⁻¹ (see Table 6) may be compared to the $\nu_{\text{C-S}}$ at 728-680 cm⁻¹ assigned by Podlaha and Podlahova⁷⁷ in dithioacetic acid complexes. As a result of comparing the vibrational spectra of sulfide and selenide complexes of platinum and palladium and their free ligands, the peaks

which shift to lower frequencies in the selenium complexes are assigned to $\nu_{\text{C-Se}}$ (see Table 6).

(b). Low Frequency Region

The cis isomer of an unsymmetrical bidentate chelate complex M(LL')_2 has C_{2v} local symmetry and should give rise to two M-S and two M-O stretching frequencies which coincide in the infrared and Raman spectra. Since the trans isomer belongs to the point group C_{2h} , only one M-S and one M-O stretching frequencies are expected. The $\nu_{\text{M-O}}$ and $\nu_{\text{M-S}}$ do not coincide in the infrared and Raman spectra because the trans isomer has a center of symmetry.

Chelated complexes usually give very complicated vibrational spectra in the low frequency region.⁷² Assignments for these systems are, therefore, difficult. However, making use of both the infrared and Raman spectra and by intercomparison of spectra of the closely related bis-chelates, the metal-ligand stretching frequencies are tentatively assigned.

Although normal coordinate analyses were employed, there are two discordant views in the literature regarding the nature of the M-O bond of amino acid complexes like bis(glycinato)platinum(II). Nakamoto⁶¹ assigned $\nu_{\text{M-O}}$ in the range 420-290 cm^{-1} by assuming a fair amount of covalent nature of the bond. However, Quagliano et al.⁷⁸ regarded the M-O bond as essentially ionic with no $\nu_{\text{M-O}}$ above $\sim 250 \text{ cm}^{-1}$.

Normal coordinate analyses have been carried out on the glycinato complexes of platinum and palladium and the assignments of metal-oxygen stretching frequency of the trans complexes at 415 cm^{-1} and 420 cm^{-1} have

been made for the platinum and palladium complexes respectively. Condrate and Nakamoto have assigned another strong band in the region 385-330 cm^{-1} as an out of plane chelate ring deformation.⁷⁹ In the present system of bis-chelates a second fairly strong band usually occurs at 410-320 cm^{-1} , which may probably arise from a similar chelate ring deformation.

For the present series of bis-chelates, it seems reasonable to assume that their metal-oxygen bonds have a fair amount of covalent character because their infrared spectra show a wide separation of anti-symmetric and symmetric carbonyl stretching frequencies and their ¹H n.m.r. spectra indicate non-labile metal-ligand bond properties in solution.

The tentatively assigned metal-ligand stretching frequencies fall in the following ranges (from Table 7):

| | Infrared | Raman | | Infrared |
|----------------------|--------------------------|--------------------------|---------------------|--------------------------|
| $\nu_{\text{Pt-O}}$ | 353-375 cm^{-1} | 397-407 cm^{-1} | $\nu_{\text{Pd-O}}$ | 369-397 cm^{-1} |
| $\nu_{\text{Pt-S}}$ | 304-320 cm^{-1} | 291-304 cm^{-1} | $\nu_{\text{Pd-S}}$ | 330-336 cm^{-1} |
| $\nu_{\text{Pt-Se}}$ | 253-267 cm^{-1} | | | |

The assignment of metal-sulfur and metal-selenium stretching frequencies is not easy because these vibrations are of weak to medium intensity in both the infrared and Raman spectra and there may have been coupling with lattice and bending modes too which occur in the same region.⁸⁰

For the platinum complexes, the fairly strong bands at 353-375 cm^{-1} in the infrared and that at 397-407 cm^{-1} in the Raman are tentatively assigned to $\nu_{\text{Pt-O}}$. For the palladium complexes, the fairly

strong bands at $369\text{--}397\text{ cm}^{-1}$ in the infrared spectra are assigned to $\nu_{\text{Pd-O}}$. These assignments are in agreement with the literature that the metal-oxygen stretching is found to be intense and broad in nature.^{63a} They also fall in the same region ($290\text{--}420\text{ cm}^{-1}$) which are assigned by Nakamoto *et al.* for the amino acid complexes $\text{M}(\text{gly})_2$ (where $\text{M}=\text{Pd}(\text{II})$, $\text{Pt}(\text{II})$, and $\text{gly}=\text{NH}_2\text{CHRCO}_2^-$).⁶¹

The non-coincidence of the $\nu_{\text{Pt-O}}$ bands in the infrared and Raman spectra for the platinum complexes suggests that they are probably trans in structure. (see Table 7).

The metal-sulfur and metal-selenium stretching frequencies reported in the literature occur in a wide range. The $\nu_{\text{Pd-S}}$ is found in the range $294\text{--}330\text{ cm}^{-1}$ for the complexes, trans- $\text{PdX}_2(\text{SR})_2$.^{25,81} The $\nu_{\text{M-S}}$ and $\nu_{\text{M-Se}}$ are assigned in the ranges $307\text{--}316\text{ cm}^{-1}$ and $219\text{--}235\text{ cm}^{-1}$ respectively for trans- $\text{MX}_2(\text{R}_2\text{Y})_2$ (where $\text{M}=\text{Pt}(\text{II})$, $\text{Pd}(\text{II})$; $\text{Y}=\text{S}$, Se ; and $\text{X}=\text{Cl}$, Br , I).⁸² The $\nu_{\text{M-Se}}$ of MX_2L (where $\text{M}=\text{Pt}(\text{II})$, $\text{Pd}(\text{II})$; $\text{L}=(\text{C}_6\text{H}_5\text{Se})_2\text{C}_3\text{H}_6$, $\text{X}=\text{Cl}$, Br) are in the range $296\text{--}314\text{ cm}^{-1}$ and $285\text{--}296\text{ cm}^{-1}$ for the Pd and Pt respectively.⁸³ The $\nu_{\text{Pd-Se}}$ of trans- $\text{MX}_2(\text{R}_1\text{R}_2\text{Se})_2$ ($\text{R}_1\text{R}_2=\text{Et}_2$, PhEt) was found in the range $205\text{--}230\text{ cm}^{-1}$.²⁵ However, in the chelated complexes higher frequencies than those described above have been assigned. For example, $\nu_{\text{M-S}}$ are assigned in the range $378\text{--}385\text{ cm}^{-1}$ for the complexes $\text{ML}'\text{X}_2$ (where $\text{M}=\text{Pd}(\text{II})$ or $\text{Pt}(\text{II})$, $\text{L}'=\text{methionine}$ or $\text{S-methyl-L-cysteine}$ and $\text{X}=\text{Cl}$ or Br) and $\nu_{\text{Pd-S}}$ at 378 cm^{-1} and $\nu_{\text{Pt-S}}$ at 375 cm^{-1} for ML_2 (where $\text{M}=\text{Pd}(\text{II})$, $\text{Pt}(\text{II})$, $\text{L}=\text{cysteine}=\text{HSCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$).⁸⁴

The infrared spectra of $(\text{Ph-SA})_2\text{Pt}$ and $(\text{Ph-SA})_2\text{Pd}$ are shown in Fig. 4 and Fig. 10a. Their spectra in the region $(600\text{--}200)\text{ cm}^{-1}$ are shown in Fig. 10b and Fig. 10c. Their spectra are fairly similar in the

Table 7

Metal-Ligand Stretching Frequencies of Bis-complexes

| Compound | Frequency (cm ⁻¹) | | | |
|--|-------------------------------|---------|-------------|---------|
| | M-O | | M-S or M-Se | |
| (Ph-SA) ₂ Pt | 353 (i.r.) | 399 (R) | 320 (i.r.) | 292 (R) |
| (o-CH ₃ -SA) ₂ Pt | 354 (i.r.) | 404 (R) | 310 (i.r.) | 304 (R) |
| (m-CH ₃ -SA) ₂ Pt | 375 (i.r.) | 407 (R) | 304 (i.r.) | 294 (R) |
| (p-CH ₃ -SA) ₂ Pt | 360 (i.r.) | 401 (R) | 311 (i.r.) | 291 (R) |
| (Ph-SeA) ₂ Pt | 359 (i.r.) | 404 (R) | 253 (i.r.) | 233 (R) |
| (p-CH ₃ -SeA) ₂ Pt | 355 (i.r.) | 404 (R) | 267 (i.r.) | 247 (R) |
| (Ph-SA) ₂ Pd | 363 (i.r.) | | 336 (i.r.) | |
| (Ph-SA) ₂ Pd · 1/2H ₂ O | 371 (i.r.) | | 291 (i.r.) | |
| (o-CH ₃ -SA) ₂ Pd | 369 (i.r.) | | 319 (i.r.) | |
| (m-CH ₃ -SA) ₂ Pd | 397 (i.r.) | | 321 (i.r.) | |
| (m-CH ₃ -SA) ₂ Pd · 1/2H ₂ O | 366 (i.r.) | | 303 (i.r.) | |
| (p-CH ₃ -SA) ₂ Pd | 396 (i.r.) | | 295 (i.r.) | |
| (Ph-SeA) ₂ Pd | 393 (i.r.) | | 272 (i.r.) | |
| (Ph-SeA) ₂ Pd · H ₂ O | 335 (i.r.) | | 260 (i.r.) | |
| (p-CH ₃ -SeA) ₂ Pd | 396 (i.r.) | | 270 (i.r.) | |
| (p-CH ₃ -SeA) ₂ Pd · 1/2H ₂ O | 377 (i.r.) | | 293 (i.r.) | |

region above 600 cm^{-1} . In the region below 600 cm^{-1} , the bands at $454\text{--}491\text{ cm}^{-1}$ are different. However, in the region below 400 cm^{-1} in which the metal-ligand stretchings are expected, the strongest bands of 353 cm^{-1} and 363 cm^{-1} observed in the platinum and palladium complexes may be tentatively assigned as $\nu_{\text{Pt-O}}$ and $\nu_{\text{Pd-O}}$ respectively. The fairly strong band at 378 cm^{-1} , which is present in the spectra of both the platinum and palladium complexes, may probably be due to some deformation mode. The presence of one metal-oxygen stretching in these compounds suggests that they are probably trans in structure.

Hooper et al. have assigned the bands at $439\text{--}491\text{ cm}^{-1}$ and $428\text{--}478\text{ cm}^{-1}$ in trans-MR₂ as skeletal deformation (where M = Pt(II), Pd(II); R = isoleucine = $\text{C}_2\text{H}_5(\text{CH}_3)\text{CHCH}(\text{NH}_2)\text{CO}_2\text{H}$ and R = valine = $(\text{CH}_3)_2\text{CHCH}(\text{NH}_2)\text{CO}_2\text{H}$ respectively). In the spectra of (Ph-SA)₂Pt and (Ph-SA)₂Pd, the bands at $454\text{--}491\text{ cm}^{-1}$ are probably due to skeletal deformation. However, the patterns of the platinum and palladium complexes at this region are different, suggesting that they are probably not identical in their conformational structure. It is possible that different conformations may give rise to different infrared patterns.

Similarly, a comparison of other platinum and palladium complexes of the same ligand allows the assignments of $\nu_{\text{Pt-O}}$ and $\nu_{\text{Pd-O}}$. Thus, the $\nu_{\text{Pt-O}}$ and $\nu_{\text{Pd-O}}$ are at 354 cm^{-1} and 369 cm^{-1} respectively for $(\text{o-CH}_3\text{-SA})_2\text{Pt}$ and $(\text{o-CH}_3\text{-SA})_2\text{Pd}$ (see Fig. 3 and Fig. 10d); at 375 cm^{-1} and 397 cm^{-1} respectively for $(\text{m-CH}_3\text{-SA})_2\text{Pt}$ and $(\text{m-CH}_3\text{-SA})_2\text{Pd}$ (see Fig. 10e and Fig. 10f); at 360 and 396 cm^{-1} respectively for $(\text{p-CH}_3\text{-SA})_2\text{Pt}$ and $(\text{p-CH}_3\text{-SA})_2\text{Pd}$ (see Fig. 5 and Fig. 9); at 360 cm^{-1} and 393 cm^{-1} respectively for $(\text{Ph-SeA})_2\text{Pt}$ and $(\text{Ph-SeA})_2\text{Pd}$ (see Fig. 6 and Fig. 8); at 355 cm^{-1} and 396 cm^{-1} res-

pectively for $(p\text{-CH}_3\text{-SeA})_2\text{Pt}$ and $(p\text{-CH}_3\text{-SeA})_2\text{Pd}$ (see Fig. 7 and Fig. 10g). The presence of one metal-oxygen stretching frequency of these complexes suggests that they probably have a trans-structure, in agreement with the conclusion drawn from the non-coincidence of the metal-oxygen stretching in the infrared and Raman spectra of the platinum complexes and the consideration that the palladium complexes have a preference for a trans-structure.

The infrared spectra of the selenium-containing complexes of platinum and palladium have fairly similar patterns throughout the range $4000\text{-}250\text{ cm}^{-1}$. Since different chelate ring conformations will give rise to different symmetry point group with respect to the chelate ring and give rise to different number of infrared active bands, the similarity between the infrared spectra of the complexes of $(\text{Ph-SeA})_2\text{Pt}$ and $(\text{Ph-SeA})_2\text{Pd}$, $(p\text{-CH}_3\text{-SeA})_2\text{Pt}$ and $(p\text{-CH}_3\text{-SeA})_2\text{Pd}$ implies that their chelate ring structures probably are similar. For the sulfur-containing complexes of platinum and palladium, their infrared patterns of the same ligand are slightly different. Also the spectra of the sulfur-containing complexes give more bands than those of the closely related selenium containing complexes.

C. Proton Magnetic Resonance Spectra (^1H n.m.r.)

The bis-complexes studied here were not soluble in non-polar solvents. They were only sparingly soluble in most of the common solvents so that the choice of solvents for the ^1H n.m.r. study was restricted. Deuterated chloroform was used whenever the solubility allowed. Otherwise, 1,1,2,2-tetrachloroethane or hexadeuterated dimethylsulfoxide were employed.

The ^1H n.m.r. data of the inner complexes $\text{M}(\text{RC}_6\text{H}_4\text{XCH}_2\text{CO}_2)_2 \cdot x\text{H}_2\text{O}$ (where $\text{M} = \text{Pd(II)}, \text{Pt(II)}$, $\text{R} = \text{H}, \text{o-CH}_3, \text{p-CH}_3, \text{m-CH}_3$, $\text{X} = \text{S}, \text{Se}$; and $\text{R} = \text{H}, \text{p-CH}_3$, $\text{X} = \text{Se}$; $x = 0, \frac{1}{2}$, or 1) are collected in Tables 8a, 8b, 8c.

Chelate formation has the effect that the methylene protons of the ligand have been substantially deshielded and become inequivalent. In addition, the $^{195}\text{Pt-X-C-H}$ ($\text{X} = \text{S}, \text{Se}$) spin coupling is evident by the presence of satellite peaks which are absent in the corresponding palladium complexes.

The ^1H n.m.r. absorption of the phenyl ring protons shifts approximately 0.30-0.75 ppm to the lower field in the chelated complex. The protons closer to the donor atoms encounter a greater down-field shift. The large shift of protons attached to an aromatic ring not directly attached to the metal ion suggests an extensive electron delocalization has taken place within the ligand-metal system. A similar effect was observed in the complex $\text{PdCl}_2(\text{mta})_2$ (where $\text{mta} = \text{o-C}_6\text{H}_4(\text{NH}_2)\text{SCH}_3$).⁸⁵

In addition to the magnetic inequivalence of the methylene protons, coordination generates chiral centers at the sulfur atom so that diastereoisomers (meso and dl) may coexist.

Two sets of AB quartets can be resolved for the methylene protons of all these bis-complexes, with the presence of satellites for the platinum complexes. They all exhibit a doublet (not necessarily of equal population) for the methyl protons, with the exception of $(\text{m-CH}_3\text{-SA})_2\text{Pd}$ which shows three peaks.

The exhibition of AB patterns by these complexes indicates that the metal-ligand bondings (both metal-oxygen and metal-sulfur or metal-selenium) are characteristically non-labile. The spectra of complexes

of NTA, MIDA and IDA i.e., amino acid of the general formula $RN(CH_2CO_2H)_2$ (where $R=CH_2CO_2H$, CH_3 and H respectively), have shown that complexes with non-labile metal-ligand bonds exhibit AB patterns while those with labile metal-ligand bonds do not exhibit AB patterns.⁸⁶ The compound, trans-Pd(Ph-SAH)₂Cl₂, in which the palladium-oxygen bonds have been ruptured, shows a singlet at chemical shift 4.22 ppm for the methylene protons.

(a) Variable Temperature ¹H n.m.r. Studies

Variable temperature ¹H n.m.r. studies of the methyl resonance region of the platinum and palladium complexes showed that the doublet of the methyl signals coalesced to a singlet at elevated temperature (for coalescence temperature see Table 8a). The doublet was restored on cooling.

Infrared and Raman spectra indicate a trans square planar structure in the solid state. If cis-trans isomerism were negligible in the solution, then, the doublet of the methyl signals might be due to a mixture of diastereoisomers (meso and dl isomers) or to different chelate ring conformations.

The existence of meso and racemic isomers of organic sulfide and selenide complexes in solution has been demonstrated by ¹H n.m.r. for $(CH_3SCH_2CH_2SCH_3)_2PtCl_2$,³⁰ $(RSCH_2CH_2SR)_2PtX_2$ (where $R=n-C_4H_9$, $n-C_3H_7$, $X=Cl$ or Br)³² and also for monodentate sulfide ligands, $(R_2S)_2PtCl_2$ (where $R_2=(PhCH_2)_2$, $(C_2H_5)_2$, $(CH_3)_2$ or $PhCH_2$, CH_3).³² At higher temperature, the coalescence phenomenon resulted from rapid inversion at the original pyramidal sulfur to give a time average planar situation. Hunter et al.,

however, interpreted the coalescence of ^1H n.m.r. signals of PdCl_2 ⁸⁷ and $\text{M}(\text{CO})_4\text{L}$ ⁸⁸ (where $\text{L} = \text{i-C}_3\text{H}_7\text{SeCH}_2\text{CH}_2\text{SeC}_3\text{H}_7$ and $\text{M} = \text{Cr, Mo, W}$) at elevated temperature as due to chelate ring inversion rather than inversion about the Se atom.

The five-membered chelate rings formed by these bis-complexes may be similar to those of the amino acid complexes.⁵⁸ Conformational analysis has predicted that the amino acid chelate ring systems are, in general, less puckered than similar diamines. The energy barrier to ring inversion is also likely to be less than for the diamines, and thus the n.m.r. spectra are much more likely to be time averaged.⁴²

The coalescence temperatures of the complexes of the present system are fairly high, above 65°C for the palladium complexes and above 90°C for the platinum complexes. Figures 11a* and 11b* show the ^1H n.m.r. spectra of the methyl protons of $(\text{p-CH}_3\text{-SA})_2\text{Pd}$, $(\text{p-CH}_3\text{-SeA})_2\text{Pd}$, $(\text{p-CH}_3\text{-SA})_2\text{Pt}$ and $(\text{m-CH}_3\text{-SA})_2\text{Pd}$ in 1,1,2,2-tetrachloroethane at various temperatures. These temperature ranges are comparable to those of $(\text{RSC}_2\text{H}_4\text{SR})\text{MX}_2$ (where $\text{X} = \text{Cl, Br}$).³² The observation of lower coalescence temperature for the palladium complexes than for the platinum complexes is also in agreement with the literature,³⁰ suggesting that the phenomenon is due to inversion at sulfur or selenium atom.

Figure 11c* shows the low temperature ^1H n.m.r. studies of $(\text{p-CH}_3\text{-SA})_2\text{Pt}$ in CD_2Cl_2 . The separation of the peaks of the methyl protons remain essentially unchanged and that of the methylene protons is only slightly widened as the temperature is lowered to -40°C . At -51°C , the spectral patterns changed. The methylene protons coalesced, and an additional peak appeared in the methyl region. At low temperature,

* For Figures 11a, 11b and 11c see the Appendix.

the ring inversion is presumably slow. The additional peak in the methyl region at low temperature is probably due to the presence of complication of conformational isomers.

The presence of chiral center at sulfur has been shown by x-ray structural study of dichloro(L-methionine)platinum(II) where there are two independent molecules in the asymmetric unit, the sulfur atoms of which have opposite chirality.⁵⁶

Cross *et al.*¹⁵⁴ have studied the variable temperature ¹H n.m.r. spectra of mixtures of trans-(Et₂S)₂Pd(Hal)₂ and Et₂S and found that the coalescence due to sulfur inversion is concentration-independent. This coalescence temperature remains invariant in a variety of non-coordinating solvents and is independent of free Et₂S. They have observed a second coalescence at higher temperature which is assigned to ligand exchange process. The coalescence due to exchange process by an associative mechanism involves both the free and complexed ligands.

The thermoisomerization of square planar cis-trans isomers is known to proceed via an intermolecular path, which requires the presence of free ligand.³⁹ For the present system of bis-complexes, the ¹H n.m.r. spectra were studied in the absence of free ligand. It may be inferred that the coalescence observed for these bis-complexes is probably not due to cis-trans isomerization. Furthermore, the variable temperature ¹H n.m.r. studies of the methyl absorptions of these bis-complexes show that the separation between the methyl peaks decreases as the temperature is raised and finally coalesces to a single peak. The two peaks reappear as the temperature is lowered below its coalescence temperature. The relative intensity of the two peaks restored is about the same as that

before coalescence at that temperature (see Fig. 11a and Fig. 11b). For the cis-trans isomerization, the coalescence phenomenon is due to the conversion of one isomer to another. The coalescence phenomenon should be an increase intensity of one peak at the expense of the other. This latter phenomenon was not observed in the variable temperature ^1H n.m.r. studies.

It is concluded that the isomers studied in these bis-complexes are probably the diastereoisomers of meso- and racemic-isomers resulting from the presence of the chiral centers at the sulfur and selenium atoms. The coalescence phenomenon at elevated temperature corresponds to a rapid inversion at the chiral center. The rapid inversion process leads to the observation of "averaged" spectra corresponding to a weighted mean of the parameters of the individual conformers. These "averaged" spectra are equivalent to a planar conformation at sulfur or selenium.

(b) Normal Probe Temperature ^1H n.m.r. Spectra

The ^1H n.m.r. spectra (see Tables 8a, 8b, 8c) of the platinum and palladium complexes in various solvents at normal probe temperatures are discussed below.

The ^1H n.m.r. spectral data of the free ligands $\text{RC}_6\text{H}_4\text{XCH}_2\text{CO}_2\text{H}$ ($\text{X}=\text{S}, \text{Se}, \text{R}=\text{CH}_3, \text{H}$) are collected in Table 8d. Their absorptions are generally at chemical shifts of 6.95-7.50 ppm (phenyl ring, multiplet), 3.43-3.73 ppm (methylene, singlet), and 2.27-2.42 ppm (methyl, singlet).

(1) ^1H n.m.r. Spectra of Platinum Complexes

The ^1H n.m.r. spectra of these Pt(II) complexes are well resolved

Table 8a

H n.m.r. sat. of bis-complexes

| Compound | Solvent | T _c (°C) | Chemical shift (ppm) vs TMS | | | | Coupling Constant (Hz) | | | | | |
|---|---|---------------------|-----------------------------|-----------------|----------------|-------------------|------------------------|-------------------|-------------------------------|-------------------------------|----------------|----------------|
| | | | CH ₃ | CH ₂ | | SO ₂ H | J _{AB} | J _{A'B'} | J _{Pe-H_A} | J _{Pe-H_B} | | |
| | | | | δ _A | δ _B | | | | | | δ _A | δ _B |
| (<i>o</i> -CH ₃ -SA) ₂ Pt | C ₂ H ₅ Cl ₄ | -91 | 2.29(1) | 4.04 | 3.56 | 3.95 | 3.68 | 7.00-8.25 | 16.8 | 16.5 | 18 | 34 |
| | " | -109 | 2.19(2.3) | | | | | | | | | |
| (<i>m</i> -CH ₃ -SA) ₂ Pt | " | -109 | 2.47(1) | 4.07 | 3.64 | 3.96 | 3.69 | 7.10-7.69 | 17.0 | 17.6 | 17 | 34 |
| | " | -109 | 2.21(2.5) | | | | | | | | | |
| (<i>p</i> -CH ₃ -SA) ₂ Pt | CCl ₄ | - | 2.43(1) | 4.17 | 3.63 | 4.02 | 3.76 | 6.86-7.90 | 16.0 | 16.5 | 17 | 33 |
| | " | - | 2.31(1.8) | | | | | | | | | |
| (<i>p</i> -CH ₃ -SA) ₂ Pt | C ₂ H ₅ Cl ₄ | -119 | 2.42(1) | 4.01 | 3.58 | 3.91 | 3.61 | 6.90-7.83 | 16.8 | 16.5 | 17 | 34 |
| | " | - | 2.29(1.9) | | | | | | | | | |
| (<i>p</i> -CH ₃ -SeA) ₂ Pt | " | - | 2.41(1) | 3.98 | 3.47 | 3.89 | 3.47 | 6.91-7.83 | 15.9 | 16.0 | -- | -- |
| | " | - | 2.31(1.6) | | | | | | | | | |
| (<i>o</i> -CH ₃ -SA) ₂ Pd | " | - | 2.54(1) | 4.26 | 3.54 | 3.99 | 3.77 | 7.30-8.24 | 16.5 | 17 | -- | -- |
| | " | - | 2.15(1.6) | | | | | | | | | |
| (<i>m</i> -CH ₃ -SA) ₂ Pd | " | -68 | 2.45 | 4.32 | 3.61 | 4.05 | 3.87 | 7.12-7.68 | 17 | 16 | -- | -- |
| | " | - | 2.40(1) | | | | | | | | | |
| (<i>p</i> -CH ₃ -SA) ₂ Pd | " | -68 | 2.19(1.3) | 4.27 | 3.59 | 4.00 | 3.84 | 6.90-7.76 | 16.5 | 16 | -- | -- |
| | " | - | 2.29(1) | | | | | | | | | |
| (Ph-SeA) ₂ Pd | " | -70 | 2.28(1.4) | 4.33 | 3.56 | 4.31 | 3.48 | 7.20-7.90 | 16 | 15.7 | -- | -- |

T_c-coalescence temperature.

* Relative intensity of the methyl group, the weaker peak is arbitrarily taken as unity.

only tentatively assigned.

Table 8b

H n.m.r. Data of Bis-complexes

| Compound | Solvent | Chemical Shift (ppm) vs TMS | | | Coupling constant (Hz) | | | |
|--|----------------------|-----------------------------|-----------------|--|--------------------------------|-------------------------------|-------------------------------|------|
| | | CH ₃ | CH ₂ | | J _{AB} | J _{Pt-H_A} | J _{Pt-H_B} | |
| (O-CH ₃ -SeA) ₂ Pt | d ₆ -DMSO | δ _A | δ _B | CH ₂ (s) ^a DMSO ^b (?) | RC ₆ H ₄ | | | |
| | | 2.50(?) | 4.30 | 3.79 | 3.33 | 7.30-8.34 | 17.2 | -- |
| | | 2.28(4) | | | | | | |
| (α-CH ₃ -SeA) ₂ Pt | " | 2.35(2) | 4.34 | 3.80 | 3.74 | 3.29 | 6.96-7.72 | 17.0 |
| | | 2.27(2) | | | | | | 16 |
| | | 2.15(1) | | | | | | 34 |
| (p-CH ₃ -SeA) ₂ Pt | " | 2.50(?) | 4.11 | 3.49 | 3.62 | 3.29 | 7.05-7.88 | 15.7 |
| | | 2.56(1) | | | | | | 23 |
| | | 2.27(1) | | | | | | 38 |
| (Ph-SeA) ₂ Pt | " | -- | 4.14 | 3.82 | 3.69 | 3.37 | 7.00-8.15 | 15.5 |

^a New singlet peaks appeared in d₆-DMSO solution.

^b New weak peaks in d₆-DMSO solution, probably due to coordinated solvent. (?) Some doubt.

only tentatively assigned.

Table 8c

1H n.m.r. Data of Bis-complexes

| Compound | Solvent | Chemical shift (ppm) | | | | | | Coupling Constant (Hz) | |
|--|------------------------------------|--------------------------------------|-----------------|----------------|--------------------------------|----------------|-----------------|-------------------------------|------|
| | | CH ₃ | CH ₂ | | RC ₆ H ₄ | | J _{AB} | J _A J _B | |
| | | | δ _A | δ _B | δ _A | δ _B | | | |
| (m-CH ₃ -SA) ₂ Pd ₂ Cl ₂ · 2H ₂ O | CDCl ₃ | 2.47 (1.5) 2.42 (1.5) 2.21 (1) | 4.39 | 3.66 | 4.10 | 3.93 | 6.98-7.78 | 16.0 | 16.5 |
| (p-CH ₃ -SA) ₂ Pd ₂ H ₂ O | " | 2.40 (1) 2.29 (1.3) | 4.39 | 3.66 | 4.11 | 3.93 | 6.90-7.89 | 17 | 16 |
| (p-CH ₃ -SeA) ₂ Pd ₂ H ₂ O | " | 2.38 (1) 2.29 (1) | 4.51 | 3.55 | 4.49 | 3.48 | 6.86-7.92 | 15 | 15 |
| (Ph-SA) ₂ Pd ₂ Cl ₂ · 2H ₂ O | " | -- | 4.46 | 3.66 | 4.14 | 3.98 | 7.26-7.88 | 16.3 | 15.9 |
| (Ph-SA) ₂ Pd | " | -- | 4.41 | 3.65 | 4.12 | 3.78 | 7.26-7.88 | 16.5 | 15.9 |
| (Ph-SA) ₂ PdCl ₂ | (CD ₃) ₂ CO | -- | 4.20 (s) | -- | -- | -- | 7.35-8.15 | -- | -- |

* s = singlet.

Table 8a
¹H n.m.r. Data^a of the Ligands^b

| Compound | Solvent | CH ₃ | CH ₂ | RC ₆ H ₄ | COOH |
|-------------------------|----------------------|-----------------|----------------------|--------------------------------|-------|
| Ph-SAH | CDCl ₃ | — | 3.62(s) | 7.14-7.55(m) | 14.85 |
| m-CH ₃ -SAH | " | 2.27(s) | 3.60(s) | 6.90-7.30(m) | 13.11 |
| p-CH ₃ -SAH | " | 2.30(s) | 3.58(s) | 6.95-7.45(m) | — |
| p-CH ₃ -SeAH | " | 2.32(s) | 3.43(s) ^c | 6.95-7.65(m) | — |
| o-CH ₃ -SAH | " | 2.42(s) | 3.62(s) | 7.10-7.50(m) | 15.47 |
| o-CH ₃ -SAH | d ₆ -DMSO | 2.30(s) | 3.73(s) | 7.00-7.50(m) | — |
| Ph-SeA Na | " | — | 3.52(s) | 7.15-7.50(m) | — |

^a Chemical shift on the low field side of TMS (TMS = zero); s = singlet, m = multiplet.

^b Ligand of general formula RC₆H₄XCH₂CO₂H (X = S, Se).

^c Coupling constant J_{Se-C-H} = 11 Hz.

and ^{195}Pt - ^1H spin coupling (^{195}Pt , $I=1/2$, 33.7% naturally abundant) results in the appearance of satellites about the main (66.3%) proton resonance. The presence of satellites indicates that any molecular reorganization via rupture of the Pt-S linkage must be slow on the n.m.r. time scale.

$(\text{p-CH}_3\text{-SA})_2\text{Pt}$ was better soluble in most solvents than the other platinum complexes. The ^1H n.m.r. spectra of $(\text{p-CH}_3\text{-SA})_2\text{Pt}$ isolated from different reaction conditions are fairly similar in appearance in CDCl_3 . However, superimposition of the spectra showed a slight shift of the position of the methylene absorption (see Fig. 11 and Table 8a). Whether this indicates any structural difference is not certain in view of the very small shift. The study of the same sample of $(\text{p-CH}_3\text{-SA})_2\text{Pt}$ in different solvents showed that the position of the methylene absorption and the chemical shift difference of the AB protons were sensitive to the solvent used while the coupling constant $J_{\text{H-C-H}}$ remain constant. Thus, comparison of ^1H n.m.r. spectra of the platinum and palladium complexes are made only in the same solvent.

^1H n.m.r. Spectra in Tetrachloroethane

The spectra of the platinum-sulfide complexes $(\text{o,m,p-CH}_3\text{-SA})_2\text{Pt}$ in 1,1,2,2-tetrachloroethane are similar, showing a doublet for the methyl absorption and two sets of AB patterns for the methylene protons. The methyl group intensity ratios (population of isomer ratio) of o,m,p-substituted complexes are approximately 2.3, 2.4 and 1.9 respectively (the lower field methyl absorption peak is arbitrarily taken as unity and the ratio is obtained from the integration ratio). Their spectra are similar (see Tables 8a, 8b, 8c). The fact that the isomer population

ratio of o,m,p-tolyl derivatives are similar indicates that steric effect does not play a major role in determining the isomer ratio. The isomer ratio of $(p\text{-CH}_3\text{-SeA})_2\text{Pt}$ is 1.6, indicating an increased population of lower field absorption isomer compared with its sulfide analogues.

Integrations of the spectra of $(o,m,p\text{-CH}_3\text{-SA})_2\text{Pt}$ and $(p\text{-CH}_3\text{-SeA})_2\text{Pt}$ of peaks at $\delta 6.9\text{--}7.9$ ppm (C_6H_4), $\delta 3.4\text{--}4.6$ ppm (CH_2) and $\delta 2.1\text{--}2.5$ ppm (CH_3) are approximately 4:2:3 and that of $(\text{Ph-SeA})_2\text{Pt}$ is approximately 5:2 for the phenyl ring and the methylene protons, in agreement with the formula.

Comparison of the sulfide and selenide complexes in 1,1,2,2-tetrachloroethane shows that the methylene absorptions are very similar among the sulfide complexes. In the sulfide complexes the two sets of AB patterns have quite different parameters. However, the two sets of AB patterns in the selenide complexes have smaller differences (see Table Ba).

^1H n.m.r. Spectra in Hexadeuterated Dimethylsulfoxide

The ^1H n.m.r. spectra of the platinum complexes in d_6 -DMSO showed that the complexes were partially decomposed. The spectral data are located in Table 6b. The spectra show only one AB quartet in the methylene region. In addition to the AB quartet, a singlet at $\delta 3.6\text{--}3.8$ ppm probably may be due to the SCH_2 group with free rotation, namely, the Pt-O linkage is ruptured and the position is occupied by a DMSO solvent molecule. An absorption at $\delta 3.3$ ppm may be tentatively assigned to the coordinated solvent, of the assignment of coordinated DMSO at $\delta 3.55$ ppm in $\text{Pt}(\text{DMSO})_2\text{Cl}_2$.⁸⁹ Free DMSO absorbs at $\delta 2.50$ ppm. The methyl region of $(m\text{-CH}_3\text{-SA})_2\text{Pt}$ in d_6 -DMSO exhibited four peaks whereas only three were observed in

($\text{o-CH}_3\text{-SA}$)₂Pt. One of these peaks was probably superimposed with the solvent absorption at 62.50 ppm because the partially deuterated DMSO peak was very intense in these cases.

The presence of an AB quartet for the methylene protons for these platinum complexes suggests that the chelated ring is partially retained in $\text{d}_6\text{-DMSO}$. One possible explanation for the spectra may be that the dimethyl sulfoxide replaces a Pt-O bond:



(ii) ^1H n.m.r. Spectra of Palladium Complexes

The ^1H n.m.r. spectra of the palladium complexes were studied in deuterated chloroform or tetrachloroethane. The spectral data are condensed in Tables 8a and 8c. The spectral patterns are similar to those of the platinum complexes. The two AB quartets are easily identified in the absence of complication by ^{195}Pt -satellites. Similarly, to that of the platinum complexes, the chemical shift difference $\Delta\nu_{\text{AB}}$ of the two methylene protons is larger in CDCl_3 than that in 1,1,2,2-tetrachloroethane. The ^1H n.m.r. spectra reported here were obtained using the hydrated complexes since these were more soluble than their anhydrous analogues. Nevertheless, whenever the solubility allowed, the ^1H n.m.r. spectrum of the anhydrous compound was checked and was found to be similar to that of the hydrated form. The difference in solubility is probably

simply due to the difference in crystal packing.

The two sets of methylene AB patterns of S-containing palladium complexes are quite different while those of the Se-complexes are almost superimposable. The spectra of the complex $(o\text{-CH}_3\text{-SA})_2\text{Pd}$ and its ligand are shown in Figs. 13 and 14 respectively.

The complex $(m\text{-CH}_3\text{-SA})_2\text{Pd}$ gave a ^1H n.m.r. spectrum which shows a splitting of the lower field methyl resonance in both CDCl_3 and 1,1,2,2-tetrachloroethane. The chemical shift difference of the split peaks is 0.05 ppm. The ^1H n.m.r. spectrum of the anhydrous compound shows the same pattern of spectra. All the three peaks are coalesced to a singlet at 70°C . in 1,1,2,2-tetrachloroethane. The small separation of chemical shift and the coalescence phenomenon suggest that the new splitting may probably arise from chelate ring conformation difference. The reason why the $(m\text{-CH}_3\text{-SA})_2\text{Pd}$ behaved differently from the other complexes is not clear.

D. Electronic Spectra

The electronic spectral absorptions of a transition metal complex may arise from the d-d transition of the metal ion, the charge transfer, or an intra-ligand transition.⁹⁰

For d^8 diamagnetic complexes there should be three spin-allowed d-d transitions, $d_{xy} \rightarrow d_{x^2-y^2}$, $d_z \rightarrow d_{x^2-y^2}$ and $d_{xz} d_{yz} \rightarrow d_{x^2-y^2}$. The aqueous solution d-d spectrum of PtCl_4^{2-} shows three bands at 21,0 kK($\epsilon 15$), 25.5kK($\epsilon 59$), 30.2kK($\epsilon 64$).³⁶

The electronic absorption spectra of the complexes of platinum and palladium in methanol and in chloroform or methylene chloride are located in Table 9.

In the platinum complexes, the absorption at 28-29kK($\log \epsilon \sim 2$).

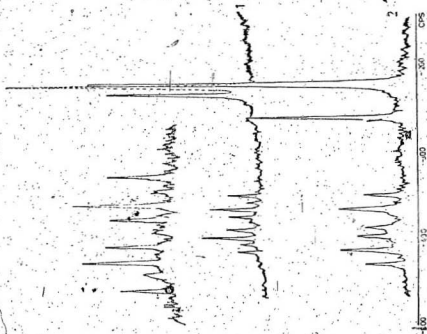


Fig. 13 100 MHz ^1H n.m.r. spectra of (1) $(o\text{-CH}_3\text{-SA})_2\text{Pt}$ and (2) $(o\text{-CH}_3\text{-SA})_2\text{Pd}$ in 1,1,2,2-tetrachloroethane.

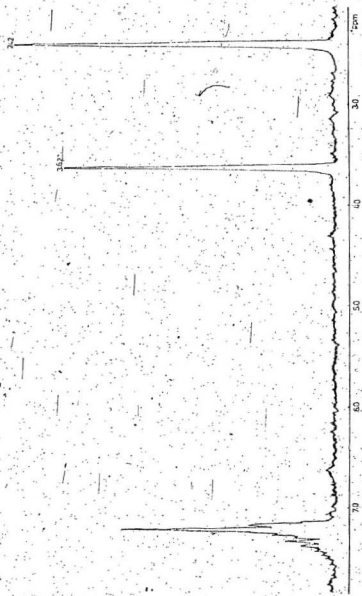


Fig. 14 60 MHz ^1H n.m.r. spectrum of $o\text{-CH}_3\text{-SA}$ in CDCl_3 .

Table 9
Electronic Spectra of Bis-complexes

| Compound | Methanol Solution | | Chloroform solution | |
|--|---|----------------------|--|----------------------|
| | Absorption Bands ^a (log ϵ) (μ K) | (λ_{\max}) | Absorption Bands (log ϵ) (μ K) | (λ_{\max}) |
| (o-CH ₃ -SA) ₂ Pt | 28.6 | (2.43) | 28.5 | (2.45) |
| | 36.0 | (3.65) | 32.7 | (3.09) |
| | 41.0 | (4.24) | 36.0 | (3.67) |
| | 44.0 | (4.37) | 40.4 | (4.24) |
| | 47.3 | (4.50) | — | — |
| (m-CH ₃ -SA) ₂ Pt | 28.6 | (2.44) | 28.5 | (2.43) |
| | 33.0 | (sh) | 32.8 | (sh) |
| | 36.3 | (3.61) | 36.2 | (4.64) |
| | 41.5 | (4.29) | 40.4 | (4.54) |
| | 46.5 | (4.45) | — | — |
| (p-CH ₃ -SA) ₂ Pt | 28.9 | (2.40) | 28.8 | (2.46) |
| | 35.7 | (3.83) | 32.9 | (sh) |
| | 41.0 | (4.35) | 35.7 | (3.59) |
| | 47.4 | (4.57) | 36.7 | (3.78) |
| | — | — | 40.3 | (4.31) |
| (Ph-SA) ₂ Pt | 28.7 | (2.25) | — | — |
| | 36.0 | (3.54) | — | — |
| | 39.5 | (4.41) | — | — |
| | 45.3 | (4.70) | — | — |
| | — | — | — | — |
| (p-CH ₃ -SbA) ₂ Pt | 28.0 | (2.32) | 27.5 | (2.16) |
| | 40.1 | (sh) | 32.5 | (2.97) |
| | 47.3 | (4.68) | 36.0 | (3.73) |
| | — | — | 40.0 | (4.30) |
| | — | — | — | — |
| (o-CH ₃ -SA) ₂ Pd | 25.0 | (3.13) | 24.9 | (2.98) |
| | 34.7 | (3.09) | 33.4 | (4.07) |
| | 43.7 | (4.28) | 42.7 | (4.15) |
| | 47.0 | (4.43) | — | — |
| | — | — | — | — |
| (m-CH ₃ -SA) ₂ Pd. 1/2H ₂ O | 24.8 | (2.14) | 24.8 | (2.96) |
| | 34.2 | (3.11) | 33.6 | (4.17) |
| | 46.7 | (4.35) | 42.0 | (4.19) |
| | — | — | — | — |
| | — | — | — | — |
| (m-CH ₃ -SA) ₂ Pd | 24.0 | — | — | — |
| | 34.1 | — | — | — |
| | 46.7 | — | — | — |
| | — | — | — | — |
| | — | — | — | — |
| (p-CH ₃ -SA) ₂ Pd. 1/2H ₂ O | 25.5 | (3.21) | 24.5 | (2.93) |
| | 33.3 | (4.32) | 32.5 | (4.03) |
| | 43.5 | (4.56) | 40.7 | (4.14) |
| | 47.1 | (4.36) | — | — |
| | — | — | — | — |
| (p-CH ₃ -SA) ₂ Pd | — | — | 24.8 | (2.90) |
| | — | — | 32.7 | (4.00) |
| | — | — | 42.7 | (4.21) |
| | — | — | — | — |
| | — | — | — | — |
| (Ph-SA) ₂ Pd. 1/2H ₂ O | 25.7 | (2.10) | — | — |
| | 34.4 | (3.14) | — | — |

Table 9 (continued)

| | | | | |
|---|-------------------|--------|------|---------------------|
| (Ph-SA) ₂ Pd.1/2H ₂ O | 44.0 | (4.26) | -- | -- |
| | 47.2 | (4.27) | -- | -- |
| (Ph-SA) ₂ Pd | 25.7 ^c | -- | -- | -- |
| | 34.5 | -- | -- | -- |
| | 44.0 | -- | -- | -- |
| | 47.1 | -- | -- | -- |
| (Ph-SeN) ₂ Pd.N ₂ O | 26.0 | (2.16) | -- | -- |
| | 33.5 | (3.97) | -- | -- |
| | 45.8 | (4.45) | -- | -- |
| (p-Cl ₃ -SeA) ₂ Pd.H ₂ O | 25.9 | (2.30) | 24.3 | (2.90) ^b |
| | 32.5 | (3.12) | 32.0 | (4.08) |
| | 43.9 | (4.36) | 42.3 | (4.22) |
| | 47.3 | (4.39) | -- | -- |
| (p-Cl ₃ -SeA) ₂ Pd | 25.9 ^c | -- | -- | -- |
| | 32.9 | -- | -- | -- |
| | 43.8 | -- | -- | -- |
| | 47.2 | -- | -- | -- |
| o-Cl ₃ -SAl | 34.6 | (2.91) | -- | -- |
| | 35.8 | (3.14) | -- | -- |
| | 40.5 | (3.76) | -- | -- |
| | 45.5 | (3.78) | -- | -- |
| o-Cl ₃ -SA K | 34.4 | (2.91) | -- | -- |
| | 35.5 | (3.10) | -- | -- |
| | 39.8 | (3.87) | -- | -- |
| | 45.8 | (3.76) | -- | -- |
| m-Cl ₃ -SAl | 34.4 | (2.77) | -- | -- |
| | 35.7 | (3.07) | -- | -- |
| | 39.5 | (3.74) | -- | -- |
| | 45.6 | (3.77) | -- | -- |
| p-Cl ₃ -SAl | 34.1 | (3.10) | -- | -- |
| | 36.5 | (3.29) | -- | -- |
| | 44.0 | (3.84) | -- | -- |
| Ph-SeA K | 37.0 | (3.51) | -- | -- |
| | 40.4 | (3.73) | -- | -- |
| | 45.9 | (3.80) | -- | -- |
| p-Cl ₃ -SeNl | 34.1 | (3.10) | -- | -- |
| | 36.5 | (3.27) | -- | -- |
| | 44.0 | (3.84) | -- | -- |

a 1'kk = 1 kilokayser = 1000 cm⁻¹.

b Electronic spectrum in dichloromethane solution.

c No extinction coefficient was determined.

is probably an absorption arising from one of the d-d transitions. The band at 36 kK (log ϵ 1.6) may be probably due to a S \rightarrow Pt charge transfer band. The free ligands also show bands in the region 34-37 kK, thus this assignment must be considered tentative only.

The absorptions at 24.9-25.8 kK (log ϵ 3) in the palladium complexes may be assigned as d-d transitions and those at 33.4-34.7 kK (log ϵ 3-4) may be due to S \rightarrow Pd charge transfer. Though log ϵ 3 for these bands might seem a little high for a $4d^8$ transition, they are in good agreement with palladium-cysteine complex Pd(L-H)₂ (where L=cysteine=HSCH₂CH(NH₂)CO₂H), where the observed maxima at 23.6 kK (log ϵ 3.4) and 31.3 kK (log ϵ 3.79) were assigned to d-d transition and S \rightarrow Pd charge transfer respectively.⁸⁴ The d-d transitions of trans-Pd(R₂S)₂X₂ (where R=n-C₄H₉, i-C₄H₉, i-C₃H₇, and X=halogens) are assigned at 22-24 kK and the S \rightarrow Pd charge transfer at about 32 kK.⁹¹ Greenwood and Hunter studied Pd(II) and Pt(II) complexes of 1,2-bis(isopropylseleno)ethane and found that the monomeric PdLCl₂ had bands at 24.05 kK (log ϵ 3.28) and 31.1 kK (log ϵ 3.40) in ethanolic solution and 23.8 kK (log ϵ 3.26) and 32.5 kK (log ϵ 3.32) in chloroform solution.⁹²

The absorption spectra of the selenium complexes show that there is not much difference between S and Se as ligating atoms. This is in agreement with the slight difference in stability constants of complexes of class "b" metals with Se and S ligands.⁹³

E. Mass Spectra

The bis-complexes studied here are not volatile. No molecular ion of the complex can be obtained from the mass spectra. Since palladium

consists of several isotopes of different natural abundance, 102 (0.96%), 104 (10.97%), 105 (22.23%), 106 (27.33%), 108 (26.71%), 110 (11.81%), the mass spectral peaks which contain palladium metal should show these relative intensity patterns. However, the mass spectra of the palladium complexes do not show the expected pattern at the higher mass number region. Therefore, the weak peaks at the higher mass number region cannot be assigned with certainty.

The major fragments of the mass spectra of the palladium complexes are similar to those of the free acids. This suggests that the metal-ligand bonds are broken prior to other fragmentations. There is not much information that could be obtained from the mass spectra.

E. X-ray Diffraction Pattern

The x-ray powder patterns were obtained using K_{α} radiation and the d-spacings are calculated by the Bragg equation:

$$\frac{d}{n} = \frac{\lambda}{2 \sin \theta}$$

where λ = x-ray wavelength (a weighted average value of 1.5417 Å is used);

d = distance between successive identical planes of atoms in the crystal;

θ = angle between the x-ray beam and these atomic planes

and n = any whole number.

The d-spacing and the relative intensity of the diffraction pattern of the complexes are located in Table 10. The diffraction patterns of the anhydrous palladium complexes indicate that the complexes are iso-morphous. However, the patterns of the (A) and the (B) forms of a compound are different too. The (A) and (B) forms of the samples of (m-CH₃-

Table 10

X-ray Diffraction Pattern

| Compound | d -Spacing (Å) | | (Relative Intensity, I/I_0) | | | | |
|--|------------------|-------------|--------------------------------|-------------|------------|------------|------------|
| (<i>o</i> -CH ₃ -SA) ₂ Pd | 4.94 (10) | 3.66 (11.5) | 3.10 (11.5) | 2.59 (6.9) | 2.27 (4.3) | 2.09 (3.3) | 1.82 (1.7) |
| (<i>m</i> -CH ₃ -SA) ₂ Pd | 4.86 (10) | 4.26 (5.0) | 3.28 (5.2) | 2.70 (5.2) | 2.44 (4.4) | 2.39 (2.5) | 2.32 (3.7) |
| | 2.25 (2.5) | 2.24 (2.5) | 2.34 (2.0) | | | | |
| (<i>p</i> -CH ₃ -SA) ₂ Pd | 5.04 (10) | 4.94 (6.8) | 4.41 (8.8) | 3.75 (11.3) | 3.56 (1.0) | 3.50 (1.5) | 2.85 (3.0) |
| | 2.66 (3.2) | 2.57 (3.7) | 2.53 (2.4) | 2.46 (3.8) | 2.32 (1.4) | 2.29 (1.7) | 2.24 (1.7) |
| | 2.17 (1.6) | 2.14 (1.4) | 2.06 (1.7) | | | | |
| (<i>p</i> -CH ₃ -SeA) ₂ Pd | 6.37 (0.3) | 6.20 (0.6) | 5.16 (4.0) | 4.69 (2.5) | 3.68 (1.6) | 3.41 (1.7) | 2.69 (5.8) |
| | 2.48 (2.8) | 2.25 (1.8) | | | | | |
| (<i>p</i> -CH ₃ -SA) ₂ Pt | 4.85 (7.0) | 4.74 (8.3) | 4.51 (2.0) | 4.32 (1.0) | 4.18 (5.0) | 4.09 (10) | 3.44 (2.0) |
| | 3.36 (2.0) | 2.72 (3.0) | 2.58 (2.0) | 2.53 (3.0) | 2.34 (2.0) | 2.06 (2.0) | 1.74 (2.0) |
| (<i>o</i> -CH ₃ -SA) ₂ Pd.1/2H ₂ O | 4.94 (10) | 4.32 (5.2) | 4.05 (1.8) | 3.32 (3.6) | 2.66 (1.4) | 2.58 (4.6) | 2.30 (2.1) |
| | 2.15 (1.3) | 2.07 (1.1) | 2.00 (1.1) | | | | |
| (<i>o</i> -CH ₃ -SA) ₂ Pd.1/2H ₂ O | 5.17 (0.5) | 4.55 (6.9) | 4.34 (9.3) | 3.30 (10) | 3.21 (2.0) | 2.67 (5.1) | 2.16 (4.0) |
| | 2.06 (1.8) | 2.03 (5.0) | 1.98 (2.5) | 1.83 (2.8) | | | |
| (<i>p</i> -CH ₃ -SA) ₂ Pd.H ₂ O | 6.20 (10) | 5.70 (10) | 5.16 (3.0) | 4.04 (2.4) | 2.17 (1.1) | 2.08 (1.1) | 2.01 (1.1) |
| | 1.84 (1.3) | 1.78 (1.4) | | | | | |
| (<i>p</i> -CH ₃ -SeA) ₂ Pd.H ₂ O | 6.37 (0.9) | 6.20 (1.3) | 4.91 (10) | 4.42 (4.2) | 4.03 (1.5) | 3.69 (2.2) | 3.54 (1.1) |
| | 2.59 (1.6) | 2.53 (1.6) | 2.25 (3.0) | 2.22 (1.5) | 1.84 (1.9) | | |

$(\text{SA})_2\text{Pd}$ and $(p\text{-CH}_3\text{-SeA})_2\text{Pd}$ are only slightly different. However, the hydrated (A) form of $(p\text{-CH}_3\text{-SA})_2\text{Pd}\cdot\text{H}_2\text{O}$ gave only a poor diffraction pattern which is quite different from its anhydrous form.

The isomorphous property among the anhydrous compounds indicates that the structures of these compounds are probably the same. For the compound $(o\text{-CH}_3\text{-SA})_2\text{Pd}$, steric effect consideration should make the trans structure more favourable. Thus, it is likely that the anhydrous palladium complexes have a trans structure in agreement with the infrared and ^1H n.m.r. evidence.

The difference in diffraction pattern between the hydrated (A) and anhydrous (B) forms may be either because (A) has a different structure or the effect of crystal packing is different in the two cases. This effect is seen in the diffraction patterns of anhydrous $(m\text{-CH}_3\text{-SA})_2\text{Pd}$. The infrared spectra of the samples of $(m\text{-CH}_3\text{-SA})_2\text{Pd}$ recrystallized from chloroform and from acetone are identical. However, the former gave a poor diffraction pattern while the latter resulted in a good one. Their patterns are also slightly different.

G. Conclusion

From the above discussion, it is concluded that the bis-complexes of platinum have a trans square planar structure and consist of two diastereomers because of the presence of chiral centers at the chalcogen atoms. The bis-complexes of palladium probably have the same structure because their spectral properties are fairly similar to those of the corresponding platinum complexes. The difference in the infrared spectra of the hydrated and anhydrous complexes of palladium is probably simply due to the

presence or absence of water in the crystal. However, the solubility of the anhydrous palladium complexes is so low that a more extensive study of them in solution was not carried out.

CHAPTER III

PLATINUM(II) AND PALLADIUM(II) COMPLEXES OF
SUBSTITUTED PHENYLSULFOXYACETIC ACIDS

Introduction

The use of sulfoxide as ligand has been widely studied since 1960 and has been reviewed.¹⁴ Infrared⁹⁴ and x-ray diffraction studies⁹⁵ of metal complexes of dimethylsulfoxide (DMSO) have shown that while dimethylsulfoxide is generally associated with metal ions through its oxygen atom, sulfur donation was favoured for some cations, such as Pt(II) and Pd(II).⁶

However, in the tetrakis(dialkylsulfoxide)palladium(II) complexes, both sulfur and oxygen bonded dialkylsulfoxide ligands are reported.⁹⁶⁻⁹⁸ Dimethylsulfoxide forms cis-[Pd(Me₂SO)₂(Me₂SO)₂]²⁺ (where donors are underlined), di-n-propylsulfoxide and di-n-butyl-sulfoxide both form trans-[Pd(R₂SO)₂(R₂SO)₂]²⁺ and di-iso-pentylsulfoxide forms an entirely oxygen-bonded cation [Pd((i-pentyl)₂SO)₄]²⁺.⁹⁸ It has been suggested that, in the absence of severe steric effects, dialkylsulfoxides exhibit their true preference for metal-sulfur bonding. Increasing the steric effects can prevent sulfur to metal bonding but still allows oxygen to metal bonding so that a mixed sulfur and oxygen bonded sulfoxide cation is obtained. In the presence of severe steric effects, only the oxygen-bonded complex is obtained.

The nature of the sulfur-oxygen bond in sulfoxide is a matter of some controversy. Double bond character has been suggested for the sulfur-oxygen linkage based on the observations of small bond moment, shorter bond length and greater bond strength than the sulfur-oxygen

single bond. However, rather small force constants, strong hydrogen bonding properties, and other parameters such as bond refraction and polarizability, have led to the conclusion that the sulfur-oxygen linkage of sulfoxides has a semi-polar character.⁹⁹ ¹H n.m.r. spectra indicate that the anisotropy of this group is more akin to that of the C≡C bond than to that of the C=O bond.¹⁰⁰

The pyramidal nature of sulfoxide sulfur renders the methylene protons in benzylmethylsulfoxide nonequivalent so that an AB pattern in the ¹H n.m.r. was observed. Furthermore, it has been shown that one of the methylene protons exchanged with deuterium 14 times as rapidly as the other.¹⁰¹ The non-equivalence of the methylene protons in the ligands m- and p-tolylsulfoxyacetic acids is expected and has been observed. As for the sulfoxide complexes, ¹H n.m.r. studies have shown that the metal-sulfur bonding is retained in the solution.^{102,103}

The donor properties of m- and p-tolylsulfoxyacetic acids are investigated here so that comparison with those of the corresponding thio ligands is possible. Although simple sulfoxides as ligands have been widely studied, it seems that no research has been done on how the presence of other competing donor groups in the same ligand will affect the donor power of sulfoxide.

Experimental Section

A. Preparation of Tolylsulfoxyacetic Acids

The ligands *m*- and *p*-tolylsulfoxyacetic acids were prepared by the method of Leonard and Johnson^{7, 104} by oxidation of the corresponding (poly)thioacetic acid with sodium metaperiodate in methanol. The method of preparation of (*m*-tolylsulfoxy)acetic acid ($m\text{-CH}_3\text{-SO-AH}$) is given below. The corresponding *p*-tolyl derivative was prepared similarly.

To a 0.50 M solution of sodium metaperiodate NaIO_4 (0.105 mole in 210 ml water) at 0°C was added dropwise (*m*-tolylthioacetic acid (0.100 mole) in 160 ml methanol. The NaIO_3 which precipitated was removed by filtration after the mixture was stirred at 0-5°C for ten hours. The chloroform extract of the filtrate, after drying over anhydrous MgSO_4 was concentrated to yield a white precipitate. Recrystallization from chloroform-petroleum ether gave the required product (138 g, 70%), m.p. 89.0-90.5°C (lit.⁷ 88.0-89.0°C).

Yield of (*p*-tolylsulfoxy)acetic acid: (89%), m.p. 105.5-106°C (lit.⁷ 105.4-105.8°C).

B. Preparation of Chelated Complexes

(i) Potassium dichloromono(*p*-tolylsulfoxyacetato)platinate(II)

An aqueous solution of potassium tetrachloroplatinate(II) (1.661 g, 4.00 mmole in 20.0 ml water) was added to an aqueous solution of potassium (*p*-tolylsulfoxy)acetate (4.00 mmole in 24.0 ml water) to give a yellow precipitate which began to form after half an hour at room temperature.

The product was recrystallized from 10% ethanol and dried at 90°C in vacuo to give the title compound (1.820 g, 91%), m.p. 254°C (dec.).

Anal. calcd. for $C_9H_9Cl_2O_3SKPt$:

| | | | | |
|-------|-----------|----------|----------|-----------|
| | C, 21.52; | H, 1.81; | S, 6.38; | Cl, 14.11 |
| Found | C, 21.71; | H, 1.94; | S, 6.56; | Cl, 13.89 |

(ii) Potassium dichloromono(m-tolylsulfoxyacetato)platinate(II)

Aqueous solutions of potassium tetrachloroplatinate(II) (1.661g, 4.00 mmole in 20.0 ml) and (m-tolylsulfoxyacetate (4.00 mmole in 24.0 ml) were mixed. A yellow precipitate began to form after eight hours at room temperature and was filtered after eleven hours. Recrystallization from 10% ethanol and drying at 90°C in vacuo gave the title compound (1.540 g, 77%), m.p. 244°C (dec.).

Anal. Calcd. for $C_9H_9Cl_2O_3SKPt$:

| | | | | |
|-------|-----------|----------|----------|-----------|
| | C, 21.52; | H, 1.81; | S, 6.38; | Cl, 14.11 |
| Found | C, 21.35; | H, 1.89; | S, 6.49; | Cl, 13.83 |

Dissolution of the product in D_2O followed by distillation of the solvent in vacuo gave the deuterated compound.

(iii) Potassium dibromomono(p-tolylsulfoxyacetato)platinate(II)

An aqueous solution of potassium tetrabromoplatinate(II) (2.00 mmole in 45.0 ml) was added to an aqueous solution of potassium(p-tolylsulfoxyacetate (2.00 mmole in 8.0 ml) to give a precipitate which was filtered after twenty-two hours at room temperature. The product was filtered off, washed with cold water and dried in vacuo at 90°C to give

the title compound (0.6525 g, 55%); m.p. 225°C (dec.).

Anal. calcd. for $C_9H_9Br_2O_3$ SKPt: %

C, 18.29; H, 1.53; S, 5.42; Br, 27.03

Found C, 18.40; H, 1.65; S, 5.52; Br, 26.98

(iv) Potassium dibromomono(m-tolylsulfoxyacetate)platinate(II)

The mixture of aqueous solution of potassium tetrabromoplatinate(II) (2.00 mmole in 45.0 ml) and potassium(m-tolylsulfoxyacetate) (2.00 mmole in 8.0 ml) was stirred at room temperature until the initial dark brown coloration disappeared. A trace of brownish decomposed residue was filtered off. The oil obtained from cooling the yellow solution was taken up in acetone. Slow evaporation of a water-acetone (1:3) solution in a vacuum desiccator yielded a yellow precipitate which was filtered, washed with cold water and dried in vacuo at -90°C to give the title compound (0.3890 g, 33%), m.p. 222°C (dec.).

Anal. calcd. for $C_9H_9Br_2O_3$ SKPt:

C, 18.29; H, 1.53; S, 5.42; Br, 27.03

Found C, 18.42; H, 1.61; S, 5.57; Br, 27.08

(v) Potassium dichloromono(p-tolylsulfoxyacetate)palladate(II)

An aqueous solution of potassium tetrachloropalladate(II) (2.00 mmole in 40.0 ml) was added slowly with stirring to an aqueous solution of potassium(p-tolylsulfoxyacetate) (2.00 mmole in 10.0 ml). A brownish yellow precipitate which formed immediately was filtered after one hour at room temperature, washed with cold water and dried in vacuo to give

the title compound (0.2367 g, 28.7%), m.p. 201°C (dec.).

Anal. calcd. for $C_9H_9Cl_2O_3SKPd$:

| | | | | |
|-------|-----------|----------|----------|-----------|
| | C, 26.13; | H, 2.19; | S, 7.75; | Cl, 17.14 |
| Found | C, 26.18; | H, 2.21; | S, 7.88; | Cl, 16.94 |

(vi) Potassium monochloro-monobromo(p-tolylsulfoxyacetato)platinate(II)

To an aqueous solution of $K[Pt(p-CH_3-SO-A)Cl_2]$ (2.00 mmole in 100 ml) was added an aqueous solution of potassium bromide (4.00 mmole in 10.0 ml). The volume of the solution was reduced to one third after one hour at 30°C. Slow evaporation of the solution in vacuum desiccator yielded the title compound, m.p. 225°C (dec.).

Anal. calcd. for $C_9H_9ClBrO_3SKPt$:

| | | | | |
|-------|-----------|----------|----------|----------|
| | C, 19.80; | H, 1.66; | S, 5.87; | Cl, 6.49 |
| Found | C, 19.57; | H, 1.80; | S, 5.86; | Cl, 4.32 |

C. Unsuccessful Attempts

(i) The reaction of $K[Pt(p-CH_3-SO-A)Cl_2]$ and potassium thiocyanate in aqueous solution yielded an insoluble gelatinous precipitate. Recrystallization was impossible due to its insoluble property. The infrared spectra showed the presence of (p-tolylsulfoxyacetate group as well as the thiocyanate group. However, no analytically pure compound was obtained.

(ii) The reaction of iodide ion (cesium iodide and lithium iodide mixture) on $K[Pt(p-CH_3-SO-A)Cl_2]$ in aqueous solution under nitrogen atmosphere caused the decomposition of the original complex. A black decomposed residue was removed after one hour and the resulting solution

yielded a green compound. The infrared spectrum of the green compound showed that the characteristic peaks of p-tolylsulfoxyacetate ligand were absent. m.p. 293°C.

(iii) The reaction of a stoichiometric amount of tetramethylammonium bromide with $K[Pt(p-CH_3-SO-A)Cl_2]$ in an aqueous solution at room temperature yielded an orange yellow precipitate. Its infrared spectrum was similar to the compound $K[Pt(p-CH_3-SO-A)ClBr]$ and showed no characteristic peak of tetramethylammonium ion at 945 cm^{-1} .

(iv) The reaction of excess tetramethylammonium bromide on $K[Pt(p-CH_3-SO-A)Cl_2]$ in an aqueous solution at 50°C yielded an oil. A yellow powder was obtained by grinding the oil with diethylether. Its infrared spectra showed that both of the chlorine atoms were being exchanged and the characteristic peak of tetramethylammonium ion at 945 cm^{-1} was present. Attempts to recrystallize the product from water-acetone were not successful because the same sticky oil formed again.

(v) The reaction of potassium tetrachloropalladate(II) and potassium m-tolylsulfoxyacetate in aqueous solution at room temperature yielded a product which was brownish yellow when it was wet but became dark brown when it was dried. Attempts to recrystallize it from nitromethane and water were not successful. Its infrared spectrum showed that the compound was bonded through oxygen of the sulfoxy group.

(vi) The reaction of potassium tetrachloropalladate(II) and potassium p-tolylsulfoxyacetate in aqueous solution produced in addition to $K[Pd(p-CH_3-SO-A)Cl_2]$ described above a similar compound to that obtained in (v) above.

(vii) The reaction of potassium tetrabromopalladate(II) and potassium

p-tolylsulfoxyacetate in aqueous solution also produced a similar compound to that in (v). No pure compound was obtained.

Results and Discussion

Arylsulfoxyacetic acid is a potential ambident ligand when acting as a monodentate ligand. It may also act as a chelating bidentate ligand. Finally, it is known that the methylene protons of the parent acid are non-equivalent from proton magnetic resonance spectra.

In order to compare the donor properties of arylsulfoxyacetic and arylthioacetic acids, they were reacted with platinum (II) and palladium(II) compound under similar conditions. Unlike the thio ligands which formed inner complexes easily as described in Chapter II, the sulfoxy ligands replaced only two halogen atoms from tetrahaloplatinate(II) or tetrachloropalladate(II) ions.

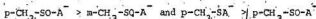
The decrease of donor property of sulfoxy ligand compared with that of the thio ligand may be attributed to the increase of effective charge on sulfoxide sulfur compared with sulfide sulfur. A higher positive charge may cause the sulfoxide to be a somewhat better π acceptor and thus be less likely to have a second sulfoxy group in the trans position. X-ray emission spectroscopy has confirmed that the effective positive charge on the sulfur atom in sulfoxide is actually higher than in the sulfide. 105, 106

Syntheses of the Complexes

Before proceeding to the discussion of the spectroscopic data, a few general comments on the preparative work are given below.

The platinum derivatives of the type $K[Pt(m,p-CH_3-SO-A)_2]$ were obtained readily from the reaction of potassium tetrahaloplatinate(II)

with the potassium salts of the sulfoxo ligand in an aqueous medium. The rate of reaction of the ligands with Pt(II) and Pd(II) decreases in the order



although no quantitative measurements of the rate of reaction have been measured. The decrease of rate of the m-tolyl ligand may be due to a decrease of electron density on sulfur atom of m-tolyl ligand compared with that of the p-tolyl ligand. The thio ligands react much faster than the corresponding sulfoxo ligands because the former have two lone pairs of electrons on the sulfur atom while the latter have only one to participate in the complex formation. In addition to the electron withdrawing effect due to the sulfur-oxygen bond, the oxygen atom of the sulfoxo group may have steric hindrance that prevents the coordination of sulfur atom to the metal.

The bromine derivatives of $\text{K}[\text{Pt}(m,p\text{-CH}_3\text{-SO-A})\text{Br}_2]$ could be prepared either from the reaction of tetrabromoplatinate(II) ion with the potassium salt of the sulfoxo ligand or by bromide exchange with the chlorine derivatives of the complex. The former method is preferred because the latter yielded a partially exchanged product and often formed an oil when tetramethylammonium bromide was used. The purification of the product from the exchange method was difficult.

When both K^+ and NMe_4^+ ions were present in an aqueous solution containing the complex ion, a crystalline product containing potassium ion as cation rather than the latter was obtained. The complex containing the tetramethylammonium ion formed a sticky oil when it was precipitated out from the solution.

The reaction of tetrahalopalladate(II) ion with the potassium salt of the ligand produced two kinds of complexes. The first type, $K[Pd(p-CH_3-SO-A)Cl_2]$, is similar to the platinum complexes. The second type was obtained when *m*-tolylsulfoxyacetate was reacted with tetrachloropalladate(II) ion or *p*-tolylsulfoxyacetate and *m*-tolylsulfoxyacetate with tetrabromopalladate(II) ion. The infrared spectra of the second type of complex show that they are bonded through the oxygen of the sulfoxide group and the carboxylate group is probably not acting as a unidentate ligand. The $\nu_a(CO_2)$ of the second type complex shifts to 1590 cm^{-1} compared with 1635 cm^{-1} for the first type and the ν_{S-O} shifts to 930 cm^{-1} from 1128 cm^{-1} . Unfortunately, attempts to purify these compounds were unsuccessful.

When $K[(p-CH_3-SO-A)PtCl_2]$ was treated with thiocyanate ion in aqueous solution, a highly insoluble compound which contains S-bonded thiocyanate group was obtained. However, no analytically pure compound could be obtained because no solvent for the product could be found.

Finally, the aqueous solution of the S-bonded chelated complexes studied here is acidic. The acidic proton could be titrated with dilute sodium hydroxide. Presumably one of the methylene protons is the acidic one.

B. Structure of the Complexes

The structural elucidation of the complexes is based on elemental analyses, the infrared, Raman, proton n.m.r. and electronic spectra, and the conductivity measurements.

Elemental analyses of the compounds are consistent with the empi-

tical representation $K[MX_2]$ (where $M=Pt(II)$, $Pd(II)$; $L=m$ - and p -tolylsulfoxyacetate and $X=Cl$ or Br). Conductivity measurements in nitromethane indicate that they are 1:1 electrolytes. The diamagnetism of these d^8 complexes suggests that they possess a square planar geometry. The complex $PdCl_2(DMSO)_2$ is definitely square planar in the solid state⁹⁵ for which magnetic susceptibility measurements⁹⁷ indicate essential diamagnetism.

(a) Infrared and Raman Spectra

(i) Higher Frequency Region

Investigation of a wide variety of sulfoxide complexes suggests that the direction of change in energy of $S-O$ stretching frequency band on coordination reflects the donor atom, i.e. S or O .¹⁴ An increase in ν_{S-O} indicates S -coordination and a decrease, O -coordination. This has been confirmed by a number of X-ray determinations.¹⁰⁷⁻¹⁰⁹ Thus $\Delta \nu_{S-O} [\nu_{S-O}(\text{ligand}) - \nu_{S-O}(\text{complex})]$ if negative indicates S -coordination, while if positive indicates O -coordination.

The electronic structure of sulfoxides may be represented by a resonance hybrid of the structures (XVII-XIX).



If coordination occurs through sulfur, the contribution of structures (XVII) and (XIX) will increase and the result may be an increase in ν_{S-O} . If coordination occurs through oxygen, the contribution of structure (XVIII) will increase and the result will be a decrease of the S-O stretching frequency. ¹¹⁰

The infrared and Raman spectra ($1800-250\text{ cm}^{-1}$) of the complex $K[Pt(p\text{-CH}_3\text{-SO-A})Cl_2]$ are shown in Fig. 15.

The infrared and Raman spectral data pertaining to the S-O and carbonyl stretching frequencies are located in Table 11. It is quite clear that the shift of the S-O stretching frequency in all the complexes $K[MLX_2]$ (where $M = Pd(II), Pt(II)$; $L = m\text{-}$ and $p\text{-tolylsulfoxyacetate}$; $X = Cl$ or Br) is negative, thus suggesting S-coordination for these complexes. The strong band at about 1120 cm^{-1} in the infrared spectra for all the complexes may be considered to derive most energy from the S-O stretching vibration. Deuterium substitution, as in the complex $K[Pt(m\text{-CH}_3\text{-SO-A})Cl_2]$, resulted in the disappearance of the bands at 1150 cm^{-1} and 1227 cm^{-1} leaving the 1120 cm^{-1} band unchanged. In the complexes $K[M(p\text{-CH}_3\text{-SO-A})X_2]$ (where $M = Pd(II), Pt(II)$; $X = Cl$ or Br), the assignment of an S-O stretching frequency is complicated by the presence of two equally strong bands at 1127 and 1117 cm^{-1} . The free ligand has a weak band at 1116 cm^{-1} . Raman spectra also show the presence of the two peaks with equal intensity at 1127 and 1118 cm^{-1} . Deuterium substitution did not shift the bands. It is known that the S-O stretching frequencies are different in conformational isomers; for example, the axial and equatorial S-O stretching frequencies of cyclic sulfite are reported at 1190 and 1230 cm^{-1} respectively. ^{111, 112} In the chelated complex, the sulfur atom is a chi-

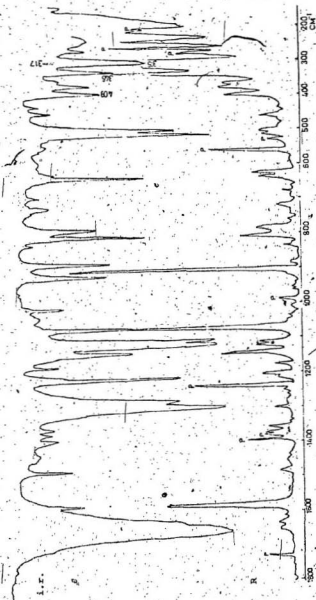


Fig. 15. Infrared and Raman spectra of $K(p\text{-CH}_3\text{-SO-A})\text{Cl}_2$.

Table 11
Infrared and Raman Data of Polyisulfoxoacetate Complexes^a

| Compound | $\nu_a(\text{CO}_2)$ | $\nu_s(\text{CO}_2)$ | $\nu_{\text{S-O}}$ | $\Delta\nu(\text{CO}_2)$ | $\Delta\nu_{\text{S-O}}$ | $\nu_{\text{C-S}}$ |
|---|---------------------------|----------------------|--------------------|--------------------------|--------------------------|--------------------|
| $\text{K}[\text{Pt}(\text{p-CH}_3\text{-SO-A})\text{Cl}_2]$ | i.r. 1665(s) R 1654(m) | 1307(s) 1307(m) | 1328(s) 1127(m) | 355 347 | -126 -125 | 726(br) 726(m) |
| $\text{K}[\text{Pt}(\text{m-CH}_3\text{-SO-A})\text{Cl}_2]$ | i.r. 1665(s) | 1310(s) | 1125(s) | 355 | -153 | 729(m) |
| $\text{K}[\text{Pt}(\text{p-CH}_3\text{-SO-A})\text{Br}_2]$ | i.r. 1655(s) | 1305(s) | 1127(s) | 350 | -125 | 725(m) |
| $\text{K}[\text{Pt}(\text{m-CH}_3\text{-SO-A})\text{Br}_2]$ | i.r. 1648(s) | 1308(s) | 1117(s) | 340 | -145 | 722(m) |
| $\text{K}[\text{Pd}(\text{p-CH}_3\text{-SO-A})\text{Cl}_2]$ | i.r. 1635(s) | 1309(s) | 1128(s) | 327 | -126 | 718(m) |
| $\text{K}[\text{Pt}(\text{p-CH}_3\text{-SO-A})\text{ClBr}]$ | i.r. 1650(s) R 1635(w) | 1308(s) 1302(w) | 1127(s) 1120(m) | 342 333 | -120 -118 | — — |
| $\text{p-CH}_3\text{-SO-NH}$ | i.r. 1712(s) | 1286(s) | 1002(s) | — | — | — |
| $\text{m-CH}_3\text{-SO-NH}$ | i.r. 1720(s) | 1270(s) | 972(s) | — | — | — |
| Ph-SO-NH | i.r. 1720(s) R 1720(w) | 1240(s) — | 1008(s) 1010(m) | — — | — — | — — |
| Ph-SO-A-Na | i.r. 1605(s) | 1365(s) | 1010(s) | 220 | — | — |

^a Infrared spectra obtained in KBr discs or nujol mull and Raman in solid powdered sample.

s = strong; m = medium; w = very.

ral center and the S-O bond may occupy either pseudo-axial or equatorial position with respect to the chelated ring. Both of the peaks at 1127 and 1118 cm^{-1} are collected in Table 11 because they cannot be assigned with certainty. However, it is possible that they arise from different conformers.

As described in Chapter II, the wide separation of the carbonyl stretching frequencies [$\Delta\nu(\text{CO}_2) \sim 355 \text{ cm}^{-1}$] compared with that of free ligands ($\sim 220 \text{ cm}^{-1}$) (see Table 11), reveals that the carboxylate group functions as a unidentate covalent ligand in these complexes.

From the above discussion, it is concluded that the arylsulfoxycarboxylate ion acts as a bidentate ligand bonded through the sulfur of the sulfoxyl group and the oxygen of the carboxylate group. The remaining two sites of the square plane are occupied by two halogen atoms.

As indicated in Chapter II, the C-S stretching bands are usually weak in intensity in the region 760-600 cm^{-1} . By intercomparison of the infrared spectra of the sulfoxyl complexes in the region 800-600 cm^{-1} and with the same region for the thio complexes, the weak bands at 730-718 cm^{-1} in these sulfoxyl complexes are tentatively assigned to C-S stretching frequencies. Since the phenyl rings have strong absorptions in this region⁷⁴ and the coordinated carboxyl group also exhibits the C=O in plane deformations in this region (e.g. 745 and 727 cm^{-1} for trans-Pt(gly)₂ and trans-Pd(gly)₂⁷⁹ respectively), the assignment of $\nu_{\text{C-S}}$ here must be considered only tentative.

(ii) Low Frequency Region

The cis-MX₂L₂ skeleton has C_{2v} symmetry at most. Both A₁ symmetric

and B_1 asymmetric stretching modes of M-X are infrared and Raman active. The symmetry of $\text{trans-MX}_2\text{L}_2$ is D_{2h} at most. The symmetric M-X stretching mode (A_g) is Raman active and the asymmetric M-X stretching (B_{3u}) is infrared active. ¹¹³

The chelated complexes $K[\text{MLX}_2]$ (where L=m- and p-tolylsulfoxyacetate, X=Cl or Br), must be cis and should yield two metal-halogen stretching modes in both the infrared and Raman spectra. The metal halogen stretching modes are easily distinguished by (a) their intensity in both the infrared and Raman spectra, (b) intercomparison of chloro and bromo derivatives and (c) comparison with data for similar molecules.

The metal-halogen and metal-sulfur stretching frequencies are collected in Table 12. A comparison of the infrared spectra of $K[\text{Pt}(p\text{-CH}_3\text{-SO-A})\text{X}_2]$ (where M=Pt(II), X=Cl, Br; and M=Pd(II), and X=Cl are shown in Fig. 16.

The position of the two metal-halogen stretching modes for compounds of the type cis- MX_2L_2 is known to vary considerably with the nature of the ligand L. ^{72, 82} The infrared spectra of all the platinum chloro derivatives show a medium intensity band at $344\text{-}339\text{ cm}^{-1}$ and a strong band at 318 cm^{-1} which may be assigned to the asymmetric and symmetric Pt-Cl stretching frequencies respectively. These strong peaks are absent in the corresponding bromo derivatives. The Raman spectrum of $K[\text{Pt}(p\text{-CH}_3\text{-SO-A})\text{Cl}_2]$ also shows the two strong bands at 346 and 317 cm^{-1} respectively. The coincidence of the Pt-Cl stretching modes in the infrared and Raman spectra as expected is in good agreement with a cis structure. These assignments are in the same region as described in, for example, cis- $\text{PtCl}_2(\text{NH}_3)_2$ (DMSO) [i.e., $346(s)$, $312(s)\text{ cm}^{-1}$] ¹¹⁴ and

Table 12
Infrared and Raman Data of Tolyisulfoxacetate Complexes

| Compound | Frequency cm^{-1} | | | | |
|---|----------------------------|---------------------|--------------------|--------------------|--|
| | $\nu_{\text{M-Cl}}$ | $\nu_{\text{M-Br}}$ | $\nu_{\text{M-O}}$ | $\nu_{\text{M-S}}$ | |
| $\text{K}[\text{Pt}(\text{p-CH}_3\text{-SO-A})\text{Cl}_2]$ | i.r. 344(m) 316(s) | -- | 406(m) | 312(sh) | |
| | R 346(m) 317(s) | -- | 406(m) | 329(sh) | |
| $\text{K}[\text{Pt}(\text{m-CH}_3\text{-SO-A})\text{Cl}_2]$ | i.r. 339(m) 317(s) | -- | 406(m) | 313(sh) | |
| $\text{K}[\text{Pt}(\text{p-CH}_3\text{-SO-A})\text{ClBr}]$ | i.r. 316(s) 318(s) | 218(m) 218(s) | 391(m) 399(mw) | 344(w) 347(mw) | |
| $\text{K}[\text{Pt}(\text{p-CH}_3\text{-SO-A})\text{Br}_2]$ | i.r. -- | 255(s) 217(s) | 395(s) | 313(w) | |
| $\text{K}[\text{Pt}(\text{m-CH}_3\text{-SO-A})\text{Br}_2]$ | i.r. -- | 245(s) 227(s) | 390(m) | 325(w) | |
| $\text{K}[\text{Pd}(\text{p-CH}_3\text{-SO-A})\text{Cl}_2]$ | i.r. 315(s) 301(s) | -- | 387(s) | 342(mw) | |

m = medium, s = strong, w = weak and sh = shoulder.

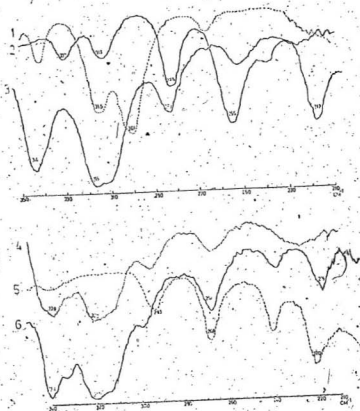


Fig. 16 Infrared spectra of (1) $K[Pd(p-CH_3-SO-A)Cl_2]$,
 (2) $K[Pt(p-CH_3-SO-A)Br_2]$, (3) $K[Pt(p-CH_3-SO-A)Cl_2]$,
 (4) $K[Pt(m-CH_3-SO-A)Cl_2]$, (5) $K[Pt(m-CH_3-SO-A)Br_2]$
 and (6) $K[Pt(Ph-SO-A)Cl_2]$.

* See ref 18.

cis-PtCl₂(Et₂S)₂ (i.r., 330(s), 320(s) cm⁻¹; Raman 331(vs), 320(sh) cm⁻¹).¹¹⁵ The strong bands of K[Pd(p-CH₃-SO-A)Cl₂] at 315 and 301 cm⁻¹ are assigned to asymmetric and symmetric Pd-Cl stretching frequencies.

Since the metal-sulfur stretching frequency also occurs in the same region as metal-chlorine stretching frequency,⁹⁷ there may have been appreciable coupling between metal-chlorine and metal-sulfur stretching frequencies in the cis complex.

The new strong bands at 255 and 217 cm⁻¹ in the infrared spectrum of K[Pt(p-CH₃-SO-A)Br₂] and 240 and 220 cm⁻¹ in that of K[Pt(m-CH₃-SO-A)Br₂] are tentatively assigned to Pt-Br stretching frequencies. These assignments fall in the same region as that of cis-PtBr₂(Et₂S)₂ (i.r., 230(s), 218(s) cm⁻¹; Raman, 230(s), 220(m) cm⁻¹).¹¹⁵ For the complex K[Pt(p-CH₃-SO-A)ClBr], the infrared peaks at 316 and 218 cm⁻¹ and the Raman peaks at 318 and 218 cm⁻¹ are assigned to Pt-Cl and Pt-Br stretching frequencies respectively.

Metal-sulfur stretching frequencies of cis-PtX₂L₂ (where L=neutral sulfide ligand) have been assigned in the range 270-350 cm⁻¹.⁷⁸ The infrared peak at 313 cm⁻¹ in the bromo-platinum derivatives and a shoulder at 313 cm⁻¹ in the chloro-platinum derivatives are tentatively assigned to Pt-S stretching frequencies. The Raman spectrum of K[Pt(p-CH₃-SO-A)Cl₂] shows a shoulder at 329 cm⁻¹ which may be assigned to Pt-S stretching frequency. However, metal-sulfur stretching bands are generally weak in intensity and they occur in the same region as metal-chlorine stretching. Various ligand skeletal bending and deformation modes further complicate the spectra in the low frequency region and the possible interaction with ligand modes which occur in the same region must make

these assignments rather tentative.

For the platinum derivatives, the peaks with moderate intensity at 404-406 cm^{-1} for the chloro derivatives and at 390-395 cm^{-1} for the bromo derivatives are assigned to Pt-O stretching frequencies. The peak at 395 cm^{-1} for the complex $\text{K}[\text{Pd}(\text{p-CH}_3\text{-SO-A})\text{Cl}_2]$ is assigned to Pd-O stretching frequency. These assignments may be compared with those reported by Kieft and Nakamoto¹¹⁶ who have assigned the peak at 388 cm^{-1} in the compound $\text{K}[\text{Pt}(\text{Gly})\text{Cl}_2]$ and the peak at 407 cm^{-1} in the compound $[\text{Pt}(\text{Gly-H})(\text{Gly})\text{Cl}]$ (where $\text{Gly-H} = \text{NH}_2\text{CH}_2\text{CO}_2\text{H}$ and $\text{Gly} = \text{NH}_2\text{CH}_2\text{CO}_2^-$) to the Pt-O stretch. The metal-oxygen stretching frequencies assigned here are in the same region as those assigned in the inner complexes described in Chapter II.

(b) Proton Magnetic Resonance Spectra

The ^1H n.m.r. spectral data are collected in Table 13. The chelated complexes studied here are insoluble in non-polar solvents. The ^1H n.m.r. spectra of the complexes taken in deuterium oxide or hexadeuterated dimethylsulfoxide only exhibit the absorption signals of methyl and phenyl groups.

The absence of the methylene group absorption suggests that the protons are completely exchanged for deuterium after dissolution. Thus the lability of the methylene protons in the chelated complexes is revealed. A similar phenomenon of labile methylene protons was observed in the palladium(II) complexes of Schiff bases derived from pyruvic acid and glycine and also from glyoxylic acid and α -alanine.¹¹⁷ The ^1H n.m.r. spectrum of $\text{Na}[\text{Pd}(\text{pyv-gly})\text{Cl}]$ (structure XX) in deuterium

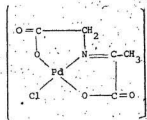
Table 1.
¹H n.m.r. Data of Tolyisulfoxacetate Complexes

| Compound ^a | Solvent | Chemical Shift (ppm) | | | | Coupling Constant (Hz) |
|--|------------------------------------|----------------------|--------------------------------|-----------------|----------------|---------------------------|
| | | CH ₃ | RC ₆ H ₄ | CH ₂ | | |
| | | | | δ _A | δ _B | |
| | | | | | | J _{AB} |
| K[Pt(p-CH ₃ -SO-A)Cl ₂] | D ₂ O | 2.48(s) ^b | 7.50-8.30(m) | — | — | — |
| K[Pt(m-CH ₃ -SO-A)Cl ₂] | " | 2.47(s) | 7.50-8.17(m) | — | — | — |
| K[Pt(o-CH ₃ -SO-A)Br ₂] | " | 2.47(s) | 7.50-8.15(m) | — | — | — |
| K[Pt(p-CH ₃ -SO-A)Br ₂] | " | 2.48(s) | 7.50-8.30(m) | — | — | — |
| K[Pd(p-CH ₃ -SO-A)Cl ₂] | " | 2.48(s) | 7.50-8.25(m) | — | — | — |
| [Pt(p-SO-AH)Cl ₂] ₂ | (CD ₃) ₂ CO | — | 7.50-8.30(m) | 4.98 | 4.44 | 15.0 |
| p-CH ₃ -SO-AH | CHCl ₃ | 2.43(s) | 7.16-7.71(m) | 3.78 | 3.12 | 14.5 |
| m-CH ₃ -SO-AH | " | 2.43(s) | 7.28-7.66(m) | 3.93 | 3.80 | 14.5 |
| Ph-SO-AH | " | — | 7.42-8.91(m) | 3.90 | 3.81 | 15.0 |

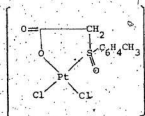
^a Abbreviation: m- and p-CH₃-SO-AH = m- and p-CH₃-C₆H₄-SOCH₂CO₂H; Ph-SO-AH = PhSOCH₂CO₂H.

^b s = singlet, m = multiplet.

oxide exhibit only the signal due to the methyl group.



XX



XXI

Structures XX and XXI show the similarity of the methylene group environments. In both cases the methylene groups are attached to two unsaturated groups. The electron density of the methylene protons is further reduced through the coordination of the donor atoms (N or S) to the metal ion. Thus, it is not surprising to see the methylene protons of the sulfoxyl chelated complex being active and easily exchanged with deuterium in deuterium oxide.

The ^1H n.m.r. spectra of the tolylsulfoxylacetic acids or their sodium salts show the following chemical shifts: a multiplet at δ 7.1-7.9 ppm (phenyl ring), an AB quartet centered at δ 3.85 ppm (CH_2) and a singlet at δ 2.43 ppm (CH_3) (see Table 13). Upon coordination to the metal, the methyl protons have been deshielded by -0.09 ppm while the ring protons ortho to the sulfoxyl group have been deshielded by as much as 0.55 ppm.

The fact that the methylene protons were easily exchanged and that the ring protons were strongly deshielded in the chelated complex

indicates that the metal-ligand bonds are probably non-labile and the complex retains its chelated form in the solution.

The ^1H n.m.r. spectrum of a chlorine-bridged complex, $[\text{Pt}(\text{Ph}-\text{SO}-\text{AH})_2\text{Cl}_2]_2$, which has been reported previously¹⁸ without the ^1H n.m.r. spectral data, will be discussed here for the purpose of comparison with the spectra of the chelated system. In the chlorine-bridged complex, the phenylsulfoxyacetate acts as a unidentate ligand bonded only via the sulfur of the sulfoxy group. Its ^1H n.m.r. spectrum in d_6 -acetone shows an AB quartet centered at δ 4.71 ppm (methylene) flanked with ^{195}Pt satellites and a multiplet at δ 7.50-8.30 ppm (phenyl ring). The methylene protons of the chlorine-bridged complex have been deshielded by -0.84 ppm upon coordination. The presence of the deshielded AB quartet with the presence of ^{195}Pt satellites indicates that the Pt-S bond is non-labile. Thus, the absence of the methylene absorptions in the chelated complexes may be because (i) the methylene protons are more active in the chelated complex and therefore more easily exchanged with deuterium and (ii) the ^1H n.m.r. spectra of the chelated complexes were recorded in D_2O making the exchange inevitable.

(c) Conductivity Measurements

The resistance (R) of a nitromethane solution of the chelated complexes in the concentration range 2×10^{-3} - 10^{-4} M at 25°C were measured. The specific conductivity $k = \text{cell constant}/R$ (where R=resistance in ohm) and the molar conductance Λ_M are related to k by the formula $\Lambda_M = 1000 k/C_M$ (where C_M =molar concentration). The molar conductances Λ_M from three or four measurements were plotted graphically as a function of $\sqrt{C_M}$. The mo-

lar conductance at the concentration $10^{-3} M$ was read directly from the graph of Λ_M vs $\sqrt{C_M}$. The values of Λ_M at $10^{-3} M$ are collected in Table 14.

Geary suggested the molar conductance Λ_M in the range $75-95 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ for 1:1 electrolytes at $10^{-3} M$ in nitromethane solution.¹¹⁸ The values of Λ_M obtained for these chelated complexes are in the range $62.9-87 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$. The Pd(II) complex was so insoluble that a more reliable value could not be obtained. Generally, the values at the lower end of the range are less reliable because these compounds were only sparingly soluble and prolonged heating at $-100^\circ C$ was required for dissolution and partial precipitation was observed at the end of the measurements. However, the electrical conducting properties of these compounds indicate that they are electrolytes. Thus, it is concluded that these chelated sulfoxo complexes are 1:1 electrolytes.

(d) Electronic Spectra

The electronic spectra of the sulfoxo complexes have no bands below 33 kK. The d-d transitions of the metal cannot be assigned because they are masked by charge transfer bands.

Jørgensen has pointed out that there is a direct correlation between the energy of a d-d transition, Dq , and the number of lone pairs on the donor atom. The lower the number of lone pairs, the higher the Dq . Thus, the anion RS^- with three lone pairs has a lower Dq than the sulfide R_2S with only two lone pairs whereas the unidentate SO_3^{2-} with one lone pair has an even higher Dq .¹¹⁹

Table 14
Molar Conductance in Nitromethane (10^{-3} M) at 25°C

| Compound | Λ_M (mho mole $^{-1}$ cm 2) |
|--------------------------------|---|
| K[Pt(p-CH $_3$ -SO-A)Cl $_2$] | 66.8 (130)* |
| K[Pt(m-CH $_3$ -SO-A)Cl $_2$] | 77.2 (130)* |
| Cs[Pt(Ph-SO-A)Cl $_2$] | 62.9** |
| K[Pt(p-CH $_3$ -SO-A)Br $_2$] | 82.2 |
| K[Pt(m-CH $_3$ -SO-A)Br $_2$] | 86.6 |
| K[Pd(p-CH $_3$ -SO-A)Cl $_2$] | 32.1 (?) |

* Conductance in aqueous solution at 10^{-2} M.

** Compound reported previously (see ref. 18).

Comparison of the electronic spectra of the thio complexes (Chapter II) and the sulfoxy complexes of the present study indicates the same general trend.

The electronic spectra of the present system agree with a square planar configuration about the platinum(II). A five-coordinate compound has a lower energy band at 20.0-28.0 kK with a molar extinction coefficient of the order of 10^3 ; this band is about 10 kK lower than the corresponding band in square planar Pt(II) complexes.¹²⁰

(e) Conclusion

The arylsulfoxyacetate ion acts as a bidentate ligand forming the chelated complexes $[MLX_2]^-$ (where M=Pt(II), L=m- and p-tolylsulfoxyacetate, X=Cl or Br; and M=Pd(II), L=p-tolylsulfoxyacetate and X=Cl). In these complexed ions, the sulfur of the sulfoxy group and the carboxylate oxygen are bonded to the metal ion forming a five-membered chelated ring. These chelated ions may be optically active because they possess asymmetric centers at the sulfur atoms. A tetrahedrally coordinated central sulfur atom bonded to four different groups may, in principle, possess chirality. An optically active complex of N-ethyl-sarcosine has been studied.¹²¹ It would be interesting to use an optically pure isomer of the ligand, which has been resolved, to synthesize the complexes and study their optical properties.

CHAPTER IV

COPPER(II) COMPLEXES OF PHENYLTHIO- AND
PHENYLSELENO-ACETIC ACIDS

Introduction

The chemistry of copper complexes in general¹²² and of the metal complexes containing sulfur, selenium and tellurium has been reviewed.¹

The stability constants of a number of thiocarboxylic acids with "hard" divalent metal ions were found to be in the order $\text{Cu} > \text{Ni} > \text{Zn}$,^{123, 124}

Ford et. al. have derived a procedure based on competing equilibria between silver and "hard" metal ions for coordination to the sulfur and selenium-containing carboxylic acids. This method is claimed to be more sensitive to coordination through the heavy donor atoms than the Bjerrum method, which is based on the proton displacement caused by complex formation between the metal ions and the substituted acids. These authors found that the complexes formed were of low stability but followed the general pattern of formation constants $\text{Cu} > \text{Co} > \text{Mn} > \text{Zn} > \text{Ni}$.¹⁶

Comparison of the stability constants of copper(II) complexes with the ligands $\text{RXCH}_2\text{CO}_2\text{H}$ (see Table 15) shows that the stabilities are in the orders $\text{alkyl} > \text{aryl}$, $\text{thio} > \text{oxy}$ and $\text{thio} > \text{seleno}$.

The [phenylthio- and phenylseleno]acetic acids form only weak complexes with copper(II) (Table 15). Yamasaki and Suzuki have reported that the sulfur atom of phenylthioacetic acid seems not to be bonded with the "hard" metal ions in their study.^{124a} By means of n.m.r. spectroscopy, McCormick et. al.¹²⁵ suggested that sulfur atom of S-methyl-L-cysteine is involved in complex formation with copper(II) while such

interaction is absent in L-methionine. X-ray study of bis(methionato)-copper(II), has confirmed that the sulfur atom is not coordinated to the copper(II) ion.¹²⁶

Table 15

The Stability Constants of Copper(II) Complexes With $RXCH_2CO_2H$

| RX = | | Ref. |
|-------------------|------------------|-----------------|
| C_2H_5O- | 62 | 123b |
| C_2H_5S- | 365 ^a | 123b |
| C_6H_5O- | 20 | 124b |
| C_6H_5S- | 31, 6 | 124b |
| C_6H_5S- | 27 | 16 _a |
| C_6H_5Se- | 19 | 16 |
| $CH_3(CH_2)_3S-$ | 90 | 16 |
| $CH_3(CH_2)_3Se-$ | 90 | 16 |

The solid metal complexes with (alkylthio)acetic acids¹²⁷ and some thiopolycarboxylic acids¹²⁸ have been studied and weak interaction of the sulfur atom in the complex formation has been suggested.

The purpose of the present study is to investigate the copper complexes of substituted (phenylthio- and (phenylseleno)acetic acids by isolating their metal complexes and to determine whether the sulfur and selenium atoms of the ligands participate in complex formation. The structure of these complexes is tentatively assigned on the basis of

magnetic moments, electronic, electron spin resonance, infrared and nuclear magnetic resonance spectra.

A brief account on the background of the electronic and electron spin resonance spectra of copper(II) complexes is given below.

Electronic Spectra

The copper(II) ion may be considered to have a $3d^9$ outer electron configuration. The effective single electron has an orbital angular momentum quantum number l equals 2. The total orbital angular momentum quantum number L equals 2 and the spin multiplicity $(2s+1)$ equals 2. Thus, copper(II) ion has a 2D ground state.

The $3d^9$ outer electron configuration of copper(II) ion lacks full cubic symmetry (that is fully regular octahedral or tetrahedral ones) and it is subject to Jahn-Teller distortion. Therefore, copper(II) yields distorted forms of the basic stereochemistry.

The way in which the d-orbitals of copper(II) ion split in an octahedral or tetrahedral crystal field is shown by the Orgel diagram ¹²⁹ in Fig. 17.

In an elongated tetragonal crystal field, the levels in the octahedral symmetry are further split. In the electronic transition, instead of the single $^2T_{2g} \leftarrow ^2E_g$ transition, which occurs for the regular octahedron, the tetragonally distorted molecule will exhibit two transitions $^2B_{2g} \leftarrow ^2B_{1g}$ and $^2E_g \leftarrow ^2B_{1g}$ at about the expected octahedral frequency. A further band at much lower energy is expected from the $^2A_{1g} \leftarrow ^2B_{1g}$ transition. ¹²⁹ (See Fig. 18.)

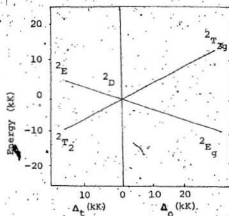


Fig. 17 Orgel diagram for octahedral and tetrahedral d^9 complexes (reproduced from ref. 129, p.126).

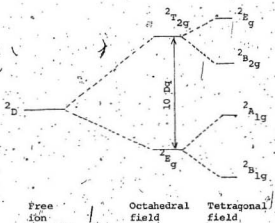


Fig. 18 Energy level scheme for d^9 octahedral complexes including Jahn-Teller splitting effects (Ref. 129 p. 179).

Electron Spin Resonance Spectra (e.s.r.)

The copper(II) ion has an effective spin of $1/2$ and associated spin angular momentum of $m_s = \pm 1/2$ leading to a doubly degenerate spin energy state in the absence of a magnetic field. The degeneracy is lifted in the magnetic field and the transitions which occur between the two levels are given by the condition

$$h\nu = g\beta H$$

For a free electron, the Landé splitting factor, g , has the value 2.0023. For an electron in a crystal field the g value may be different in different environments. g is isotropic in a cubic environment; in axial and rhombic crystal fields two and three different g -values are obtained respectively.¹³⁰

The e.s.r. spectra of magnetically concentrated copper(II) complexes, for example, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ show strong exchange interaction between isolated pairs of Cu(II) ions and give both low and high field spectra. The magnetically dilute systems give a rather more simple e.s.r. spectra.

The e.s.r. spectra due to uncoupled copper(II) complexes in an axial symmetry can be described by the spin Hamiltonian

$$\mathcal{H} = g_{\parallel} \beta H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y) + A S_z I_z + B (S_x I_x + S_y I_y)$$

where β is the Bohr magneton, H is the magnetic field, $S(\pm 1/2)$ is the effective electron spin, $I(\pm 3/2)$ is the nuclear spin, g_{\parallel} and g_{\perp} are the electronic g factors parallel and perpendicular to the z axis, A and B are the hyperfine interaction parameters parallel and perpendicular to the z axis. The behaviour of the energy levels is illustrated schematically.

tically in Fig. 19.¹³¹ Thus, an uncoupled copper(II) complex gives rise to four hyperfine lines corresponding to the selection rule $\Delta M_I = 0$ and

$$\Delta M_S = \pm 1.$$

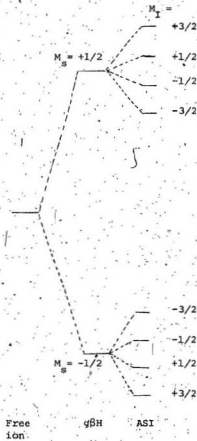


Fig.19 Energy levels of a copper(II) ion ($S=1/2$, $I=3/2$) in an applied field.

Experimental Section

Preparation of Copper(II) Complexes(1) Bis(phenylthioacetato)copper(II) (Ph-SA)₂CuMethod (a)

An aqueous solution of sodium(phenylthioacetate) (1.14 g, 6.00 mmole in 37.0 ml water) was added slowly to a warm aqueous solution of copper(II) bromide (0.670 g, 3.00 mmole in 15.0 ml water). A green precipitate formed immediately. The residue was extracted with chloroform to give a green solution, from which the required product was isolated; 0.168 g (14.1%), m.p. 147.5-8.5°C

Anal. calcd. for $C_{16}H_{14}O_4S_2Cu$:

| | | | | |
|-------|----------|---------|----------|----------|
| | C, 48.29 | H, 3.55 | S, 16.11 | Cu, 15.9 |
| Found | C, 48.23 | H, 3.51 | S, 16.12 | Cu, 16.1 |

In addition to the above product, a chloroform insoluble product which was probably a hydrated compound was also obtained from the reaction residue; 0.330 g, m.p. 133-34°C (dehydr.).

Anal. calcd. for $C_{16}H_{14}O_4S_2Cu \cdot 2H_2O$: Cu, 14.6

Found Cu, 14.8

Method (b)

An alcoholic solution of(phenylthioacetic acid (5.04 g, 30.0 mmole in 20.0 ml 95% alcohol) was added to an aqueous suspension of basic copper carbonate (1.11 g, 5.00 mmole in 160 ml water). The mixture was

refluxed for one hour and the resultant precipitate was dissolved in absolute alcohol. After removal of the alcohol, the residue was repeatedly recrystallized from benzene and finally from dichloroethane to yield a product which has identical infrared spectra and melting point to bis-(phenylthioacetato)copper(II); 1.57 g (26.3%).

(ii) Bis(m-tolylthioacetato)copper(II) (m-CH₃-SA)₂Cu

An alcoholic solution of (m-tolylthioacetic acid (1.82 g, 10.0 mmole in 12.0 ml 95% alcohol) was added slowly to an aqueous suspension of basic copper carbonate (0.553 g, 2.50 mmole in 100 ml water). The mixture was refluxed for one hour and the resultant green precipitate was extracted with chloroform. The chloroform was removed under reduced pressure and the residue recrystallized from diethylether to yield the title compound; 0.831 g (39.0%), m.p. 108-9°C.

Anal. Calcd. for C₁₈H₁₈O₄S₂Cu:

| | | | | |
|-------|----------|---------|----------|----------|
| | C, 50.75 | H, 4.26 | S, 15.05 | Cu, 14.9 |
| Found | C, 50.60 | H, 4.33 | S, 15.00 | Cu, 14.7 |

(iii) Bis(p-tolylthioacetato)copper(II) (p-CH₃-SA)₂Cu

An alcoholic solution of (p-tolylthioacetic acid (3.64 g, 20.0 mmole in 18.0 ml) was added to an aqueous suspension of basic copper carbonate (1.11 g, 5.00 mmole in 200 ml water). The mixture was refluxed for one hour and the resultant precipitate was extracted with chloroform. After removal of the chloroform, the green residue was repeatedly recrystallized from dichloroethane to give the title compound; 0.862 g

(20.2%); m.p. 138-9°C.

Anal. calcd. for $C_{18}H_{18}O_4S_2Cu$:

| | | | | |
|-------|----------|---------|----------|----------|
| | C, 50.75 | H, 4.26 | S, 15.05 | Cu, 14.9 |
| Found | C, 50.92 | H, 4.36 | S, 14.97 | Cu, 14.8 |

(iv) Bis(p-tolylselenoacetato)copper(II) (p-CH₃-SeA)₂Cu

An alcoholic solution of p-tolylselenoacetic acid (2.29 g, 10.0 mmole in 40.0 ml absolute alcohol) was added to an alcoholic solution of bis(acetato)copper(II)monohydrate (0.998 g, 5.00 mmole in 70.0 ml absolute alcohol). The mixture was refluxed for 2½ hours under nitrogen atmosphere. After the alcohol was removed under reduced pressure, the green residue was repeatedly recrystallized from dichloroethane to give the title compound; 1.03 g (39.6%); m.p. 161-2°C.

Anal. calcd. for $C_{18}H_{18}O_4Se_2Cu$:

| | | | | |
|-------|----------|---------|-----------|----------|
| | C, 41.59 | H, 3.49 | Se, 30.38 | Cu, 12.2 |
| Found | C, 41.43 | H, 3.30 | Se, 30.42 | Cu, 12.6 |

(v) Bis(phenylsulfoxoacetato)copper(II) (Ph-SO-A)₂Cu

An alcoholic solution of phenylsulfoxoacetic acid (1.82 g, 10.0 mmole in 70.0 ml absolute alcohol) was added to a solution of bis(acetato)copper(II)monohydrate (0.998 g, 5.00 mmole in 30.0 ml absolute alcohol). The mixture was refluxed for four hours under nitrogen atmosphere. After the alcohol was removed, the pale blue residue was recrystallized from dichloroethane to give the title compound; 1.12 g (52.6%); m.p. 135-6°C.

Anal. calcd. for $C_{16}H_{14}O_6S_2Cu$:

Cu, 14.9

Found

Cu, 14.6

Results and Discussion

The copper(II) complexes of the general formula $(RC_6H_4XCH_2CO_2)_2Cu$ ($R=H$, $m-CH_3$, $p-CH_3$, $X=S$; $R=p-CH_3$, $X=Se$) are isolated and examined by physical methods. The results are discussed below.

A. Magnetic Moments

The effective magnetic moments of the complexes, which are calculated by $\mu_{eff} = 2.84 \sqrt{\chi_M^{corr} T}$,¹³² are in the range 1.79-2.06 B.M. at room temperature (Table I6). The observation of a normal magnetic moment indicates that the copper(II) complexes studied here are magnetically dilute. They have no major interaction between the unpaired electrons on different copper ions. The magnetically concentrated bis(acetato)-copper(II) monohydrate has a magnetic moment value of 1.39 B.M.¹³² This phenomenon is caused by the spin-spin interaction between copper(II) ions. The mechanism of this interaction may involve a direct copper-copper bond or a super-exchange mechanism via a bridging acetate ligand.¹³²

Although bis(thioacetato)copper(II) is diamagnetic,¹³³ the magnetic moments of the complexes of the present study are comparable to those of substituted bis(phenoxyacetato)copper(II) dihydrate, which have μ_{eff} at 1.84-1.94 B.M.¹³⁴ Crystallographic study of bis(phenoxyacetato)-copper(II) dihydrate shows that each copper atom is coordinated to two phenoxy-oxygen atoms, two carboxy-oxygen atoms and two aquo-ligands, forming an elongated tetragonal distortion of the octahedron. The copper-phenoxy-oxygen bonds are the long bonds.¹⁵¹

Table 16
Magnetic Moments and E.S.R. Spectra of Copper(II) Complexes^a

| Compound | $\mu_{\text{eff}}(\text{B.M.})^c$ | g_a^b | g_b^b | $A \times 10^4 \text{ cm}^{-1}$ | G |
|--|-----------------------------------|---------|---------|---------------------------------|------|
| $(\text{Ph-SAl})_2\text{Cu}$ | 1.93 | 2.076 | 2.366 | 133 | 4.77 |
| $(p\text{-CH}_3\text{-SA})_2\text{Cu}$ | 1.83 | 2.077 | 2.366 | 133 | 4.77 |
| $(m\text{-CH}_3\text{-SA})_2\text{Cu}$ | 2.06 | 2.076 | 2.366 | 137 | 4.79 |
| $(p\text{-CH}_3\text{-SA})_2\text{Cu}$ | 1.80 | 2.076 | 2.368 | 138 | 4.74 |
| $(\text{Ph-SO-Al})_2\text{Cu}$ | 1.47 ^d | 2.074 | 2.354 | 151 | 4.76 |

^a Magnetic moments were measured as solid powder and e.s.r. spectra were taken in

-5×10^{-2} N methanol solution at -123 K.

^b The strong band in the e.s.r. spectrum gives the g_1 while the weak absorption bands give the g_2 .

^c For the method of obtaining the $\mu_{\text{eff}}(\text{B.M.})$, see the appendix on page 146.

^d The datum $\mu_{\text{eff}}=1.47$ B.M. is included for general reference, it is not included in the discussion section.

B. Electronic Spectra

The absorption electronic spectra of the copper(II) complexes were taken in the solid as nujol mulls and in solution in methanol or chloroform. The data are located in Table 17.

These copper(II) complexes show one broad band or two poorly resolved bands in the visible region around 11.4-14.7 kK in both the solid state and in solution. The position of the d-d bands in the solution are similar to those in the solid state.

Regular octahedral structure of copper(II) is not common. The octahedral copper(II) complexes are apt to be deformed by the Jahn-Teller effect, the d-d band (${}^2T_{2g} \leftarrow {}^2E_g$) is broadened. For a tetrahedral complex, the intensity of the d-d bands is high because of d-p mixing.

It was found that the molar intensity of the distorted tetrahedral CuX_4^{2-} (where X=halogen) was ~100 fold more intense than the corresponding octahedral hexa-aquo complexes.^{135e} Furthermore, the magnitude (~5.0 kK) of the ligand field parameter is lower than that for octahedral compounds. The square planar copper(II) complexes, bis(acetylacetonato)copper(II) for example, show two bands of nearly equal intensities in the visible region, about 15.0 and 18.0 kK; they are identified as the ${}^2A_{1g} \leftarrow {}^2B_{1g}$ and ${}^2E_g \leftarrow {}^2B_{1g}$ bands respectively.^{135b}

Hathaway et al.¹³⁰ has illustrated the variation of the appearance of electronic reflectance spectra with the various stereochemistries of copper(II) compounds. They have also noted that not only do the spectra depend upon stereochemistry, but for a given stereochemistry, the spectra vary with the value of 10 Dq and with the extent of the tetragonal

Table 17
Electronic Spectra of Copper(II) Complexes

| Compound | Solvent | Solution Spectra | | Solid Mull Spectra |
|--|--------------------|-----------------------|----------------------|-----------------------|
| | | Absorption bands (mμ) | log ε _{max} | Absorption bands (mμ) |
| (Ph-SA) ₂ Cu | CHCl ₃ | 14.0 | 2.00 | 13.3 |
| | | 26.3 | 2.60 | 11.4 |
| | | 30.5 | 2.92 | |
| | | 33.8 | 3.17 | |
| (m-CH ₃ -SA) ₂ Cu | " | 14.0 | 2.19 | 13.3 |
| | | 24.5 | 2.82 | 11.1 |
| | | 30.0 | 3.13 | |
| | | 34.0 | 3.43 | |
| (p-CH ₃ -SA) ₂ Cu | " | 13.8 | 2.10 | 13.3 |
| | | 25.5 | 2.76 | |
| | | 30.5 | 3.08 | |
| | | 34.0 | 3.20 | |
| (p-CH ₃ -SeA) ₂ Cu | CH ₃ OH | 13.9 | 2.08 | 14.8 |
| | | 26.0 | 2.67 | |
| | | 30.0 | 3.00 | |
| | | 36.5 | 3.92 | |
| | | 40.5 | 4.21 | |
| | | 45.0 | 4.37 | |
| (Ph-SO-A) ₂ Cu | " | 13.1 | 1.67 | 13.9 |
| | | 36.7 | 2.51 | |
| | | 41.7 | 3.08 | |
| | | 47.5 | 3.31 | |

distortion.^{130, 155a} Dennard *et al.* suggested the extinction coefficients of 20-50 for tetragonal fields to 100-400 for tetrahedral fields.¹⁵⁶

The d-d bands around 11.4-14.7 kK with $\log \epsilon \approx 2$ observed for these complexes suggests few possibilities for the stereochemistries around the copper(II). From the e.s.r. data (*vide infra*), the ground state of these copper(II) complexes is $d_{x^2-y^2}$ or d_{xy} .

The observed d-d transitions of these complexes may be compared with the single crystal electronic spectra of bis(ethoxyacetato)copper(II)-dihydrate, which show maxima of the x, y, and z polarizations at 13.7, 13.3 and 11.3 kK respectively.¹³⁶ The structure of bis(ethoxyacetato)-copper(II) dihydrate has been determined to be an elongated tetragonal octahedron.¹³⁷

If these copper(II) complexes are six-coordination derivatives, the sulfur or selenium atoms probably participate in the chelate formation and their coordination polyhedron must be completed by some intermolecular interaction probably through carboxyl oxygens from the neighbour. This type of coordination has been found in many complexes. For example, an x-ray structural determination of bis(methioninato)copper(II) showed that the complex had a distorted octahedral structure around the copper(II) ion. One oxygen of the carboxylate group and the amino nitrogen are bonded to the copper(II) ion in an almost planar configuration, the octahedral coordination being completed by a long copper-oxygen bond to the other carboxylate oxygen. There was no sulfur metal interaction.¹⁵⁷

If these complexes are four-coordination derivatives, in which the sulfur or selenium atoms are not coordinated, a possible stereochemistry is a compressed tetrahedral structure (ground state d_{xy}). Hathaway has indicated that the compressed tetrahedral CuN_4 may have d-d bands in the

range 12-16 kK.¹⁵⁸ The pseudo tetrahedral bis(N-isopropylsalicylidene-aminato)copper(II) complex has bands at 8.5 kK and 13.5 kK assigned as ${}^2E \leftarrow {}^2B_2$ and ${}^2A_1 \leftarrow {}^2B_2$ respectively.¹⁵⁹ The other possible stereochemistry for four coordination complexes is square coplanar. The reflectance spectrum¹⁰⁰ of a square coplanar complex of copper(II), $(\text{Pt}(\text{NH}_3)_4)(\text{CuCl}_4)$, the structure of which has been determined by x-ray crystallography,¹⁶¹ shows bands at 14.3 kK, 13.1 kK, and ~10.9 kK.

With the informations available, the structure around the copper(II) ion of these complexes is still uncertain.

C. Electron Spin Resonance Spectra (e.s.r.)

The e.s.r. data for the copper(II) complexes are located in Table 16. The spectra were measured by recording the first derivative signal as the field was scanned. Calibration was achieved by using a speck of 1,1-diphenyl-2-picrylhydrazyl (DPPH) on the tube. The DPPH, which has a g-value of 2.0036 fixes the field at one point on the chart. The magnetic field was measured by using a proton resonance meter. The field was calculated by using the accurately known relationship between the field and the frequency of the proton resonance.

$$H_{(\text{gauss})} = 2.3487 \times 10^{-4} \text{ (Hz)}$$

The g-value of the sample may be calculated by the relation

$$g = \frac{h\nu}{\beta H} = \frac{g(\text{DPPH}) \times H(\text{DPPH})}{H}$$

where g and H are the g-value and magnetic field of the sample, and $g(\text{DPPH})$ and $H(\text{DPPH})$ are those of the DPPH calibrant. The hyperfine coupling constant was obtained by measuring the field separation of the hyperfine peaks and solved by using the relation

$$A = \Delta H g \beta$$

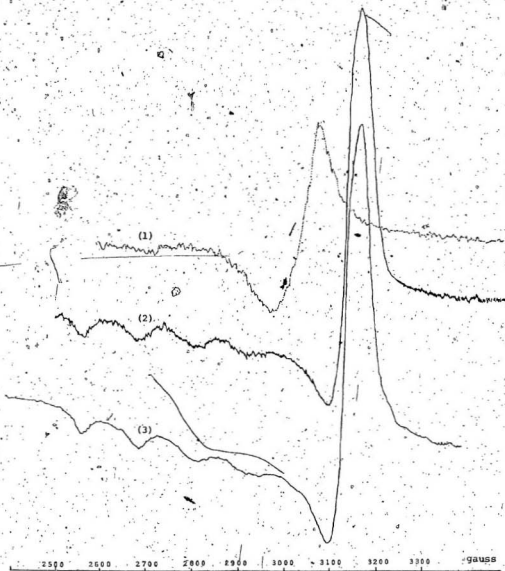


Fig. 20. E.s.r. spectra of (1) $(p\text{-CH}_3\text{-SA})_2\text{Cu}$ at room temperature, (2) $(p\text{-CH}_3\text{-SA})_2\text{Cu}$ at 123 K, and (3) $(m\text{-CH}_3\text{-SA})_2\text{Cu}$ at 123 K in 0.050 M methanol solution.

where β is the Bohr magneton, ($\beta = \frac{e}{4\pi mc^2} = 4.6686 \times 10^{-5} \text{ cm}^{-1} \text{ gauss}^{-1}$) and thus the coupling constant A has the unit cm^{-1} .

The e.s.r. spectra of an undiluted powder and methanol solution of these copper(II) complexes show a broad peak of isotropic g -value at room temperature. In the vitreous state at about 123 K axial spectra are observed (see Fig. 20). They show resonances in positions expected for mononuclear copper(II) species in agreement with the magnetic moment measurements. Thus, significant metal-metal interactions of bis(acetato)-copper(II)monohydrate type do not exist in these complexes. The resolved hyperfine splitting shows only the four lines expected for interaction of an uncoupled electron with a single copper nucleus and also there is no low field absorption observed. For the dimeric structure of bis(acetato)copper(II)monohydrate, the e.s.r. spectrum shows both high and low field absorptions. The low field components at ~1500 gauss are attributed to $\Delta M_I = 2$ transitions arising from dipole-dipole interaction between the pairs of copper(II) ions which are part of the dimeric structure.¹³⁸

The possible one electron orbital ground states of the copper(II) ion may be distinguished from the e.s.r. spectra. A $d_{x^2-y^2}$ (or d_{xy}) ground state gives a spectrum with $g_{\parallel} > g_{\perp} > 2.04$ in most cases whilst a d_{z^2} ground state usually gives a spectrum with $g_{\perp} > g_{\parallel} \approx 2.00$. The ground states for the known stereochemistries of the copper(II) ion are listed below.¹³⁰

Ground state

$d_{x^2-y^2}$

Stereochemistry

elongated tetragonal octahedral
square coplanar
elongated rhombic octahedral
square pyramidal

$d_{x^2-y^2}$

compressed tetragonal octahedral
 compressed rhombic octahedral
 linear

trigonal bipyramidal

cis-distorted octahedral

 d_{xy}

compressed tetrahedral
 square coplanar-Cu(acac)₂ type.

The g-values observed for these complexes satisfy the requirement

$g_{\parallel} > g_{\perp} > 2.04$, thus suggesting a $d_{x^2-y^2}^2$ (or d_{xy}) ground state. Since the d_{xy} ground state is known to be confined to square coplanar complexes involving chelate ligands with π -bonding potential, as in Cu(acac)₂ and compressed tetrahedral, the ground state for these complexes may be $d_{x^2-y^2}^2$. In fact, the most common stereochemistry of copper(II) complexes is a distorted octahedron which involves a $d_{x^2-y^2}^2$ ground state.

For copper(II) complexes in tetragonal distortion, the g-values for the copper(II) ions with a $^2B_{1g}$ ground state are given by the expression¹³⁹

$$g_{\perp} = 2 - \frac{2K_{\perp}^2 \lambda}{E(^2E_g \leftarrow ^2B_{1g})}$$

and

$$g_{\parallel} = 2 - \frac{8K_{\parallel}^2 \lambda}{E(^2B_{2g} \leftarrow ^2B_{1g})}$$

where K is the orbital reduction factor and λ is the spin-orbit coupling constant, which for the free ions equals 829 cm⁻¹. Hathaway et al. have defined the term G using the expression¹⁴⁰

$$G = \frac{4K_{\parallel}^2}{K_{\perp}} \cdot \frac{E(^2E_g \leftarrow ^2B_{1g})}{E(^2B_{2g} \leftarrow ^2B_{1g})} = \frac{g_{\parallel} - 2}{g_{\perp} - 2}$$

and stated that for two g-value e.s.r. spectra with the lowest g value greater than 2.04, if the value of G is 4.0-4.5, exchange coupling is negligible; for G=3.5-5.0, exchange coupling may be small and the observed g-values meaningful. For G-values outside the range 3.5-5.0; exchange coupling invalidates the observed g-values.^{130, 140}

Therefore, the observed G-value of ~4.8 for these copper(II) complexes indicates that the exchange coupling is small.

The e.s.r. data of these complexes may be compared with those of bis(ethoxyacetato)copper(II) dihydrate and bis(phenoxycetato)copper(II) dihydrate. The single crystal e.s.r. spectra of the former give g_1 , g_2 and g_3 to be 2.063, 2.088 and 2.368 respectively¹³⁶ and those of the latter are 2.061, 2.068 and 2.353 respectively.¹⁴¹

The g-values of the complexes of present study are comparable to the values of those known compounds described above. However, only two g-values instead of three are observed in these copper(II) complexes. This is not surprising, for $\text{Cu}(\text{NH}_3)_4(\text{CuI}_2)_2$ has a two g-value powder e.s.r. spectrum ($g = 2.054$, $g = 2.219$ and $G = 4.21$), but gives a three g-value single crystal e.s.r. spectrum ($g_1 = 2.054$, $g_2 = 2.058$ and $g_3 = 2.223$).¹⁴²

D. Infrared Spectra

The infrared spectra of these complexes give the asymmetric and symmetric carbonyl stretching bands at about $1580\text{--}1610\text{ cm}^{-1}$ and $1385\text{--}1400\text{ cm}^{-1}$ respectively. (See Table 18.) These values are comparable to those of glycinate and other amino acid complexes, for example, trans-bis(glycinato)copper(II) gives the asymmetric and symmetric carbonyl stretching at 1593 cm^{-1} and 1392 cm^{-1} respectively⁷⁹ and cis-bis-

Table 18
Infrared Spectra of Copper(II) Complexes^a

| Compound | Frequency cm ⁻¹ | | |
|--|----------------------------|---------------|--------|
| | ν (COO) | ν S (COO) | Cu-O |
| (Ph-SA) ₂ Cu | 1600(s) | 1400(s) | 350(m) |
| (p-CH ₃ -SA) ₂ Cu | 1580(s) | 1390(s) | 370(m) |
| (m-CH ₃ -SA) ₂ Cu | 1600(s) | 1390(s) | 355(m) |
| (p-CH ₃ -SeA) ₂ Cu | 1580(s) | 1385(s) | 370(m) |
| (Ph-SO-A) ₂ Cu | 1618(s) | 1415(s) | — |

^a Infrared spectra in KBr discs and nujol mull.

(glycinato)copper(II) monohydrate gives the antisymmetric and symmetric carboxyl stretching at 1595 cm^{-1} and 1389 cm^{-1} respectively.⁷⁹ The structure of cis-bis(glycinato)copper(II) monohydrate has been determined by x-ray to be a tetragonally distorted octahedron with two long Cu-O bonds.¹⁴³

Whether the chalcogen atoms in these copper(II) complexes participate in chelate formation is not clear from the infrared spectral data in the $4000\text{--}600\text{ cm}^{-1}$ region, because the S and Se atoms in sulfide and selenide type compounds do not give strong bands in this region and so it is difficult to distinguish them from other bands.

A comparison of the carboxyl stretching frequencies with those of the free ions shows that the $\Delta\nu(\text{CO}_2)$ of these complexes is comparable to that of the free ions. Since these complexes are soluble in organic solvents, such as chloroform, the copper-oxygen bond is probably not of ionic character as in the free ion. The small separation of the antisymmetric and symmetric carboxyl stretching frequencies indicates that the carboxylate group probably acts as a bidentate ligand bonded either to one copper ion or to two copper ions.

The Cu-O stretching frequency of pyridine-1-oxide complexes are found at about 400 cm^{-1} and 450 cm^{-1} .¹⁴⁴ The $\nu_{\text{Cu-O}}$ bands of the (alkylthio)acetato complexes are assigned in the region $360\text{--}410\text{ cm}^{-1}$.^{127b} In the complexes of the present study, a broad band at $350\text{--}370\text{ cm}^{-1}$ may be

tentatively assigned to $\nu_{\text{Cu-O}}$.

The metal-sulfur stretching band of the first row transition metals have been reported to occur over a wide frequency range.¹⁴⁵ The bands of monothio- or dithio- β -diketonates occur at about 350 cm^{-1} , while the bands occur in the range of $298\text{--}205\text{ cm}^{-1}$ in the cases of thiourea adducts.¹⁴⁶ The Cu-S bands of the copper(II) complexes studied here may be weak, therefore, no attempt of assignment of these peaks is made.

E. Nuclear Magnetic Resonance Spectra (n.m.r.)

The use of n.m.r. spectroscopy for the elucidation of binding sites of metals on amino acids is a well-established technique.¹⁴⁸ The copper(II) ion, being paramagnetic, causes proton relaxation effects and selectively broadens the signals of protons near the binding sites.^{147, 148}

The ^1H n.m.r. spectra of (ethylthio)acetic acid with copper(II) ion show that the proton signal of the methylene group adjacent to the carboxylic group is more and more broadened as the amount of copper(II) ion is increased. The proton signal of the methylene group lying between the thio and methyl groups is even more broadened than that of the methylene singlet of the acetate group. However, the methyl group is only slightly broadened as the copper(II) concentration is increased.¹⁴⁹ This result has been used to confirm the bidentate property of (ethylthio)acetic acid.¹⁵⁰

In the present study, the ^1H n.m.r. spectra of 1:2 copper(II) complexes with (tolylthio)acetic acids and (tolylseleno)acetic acid were

taken in hexadeuterated dimethylsulfoxide (Table 19). The signal of the methylene protons is so broad that it disappears from the spectra. The signal of the methyl protons occurs in the same region as that of partially deuterated dimethylsulfoxide impurity. However, the signal of methyl group at ~ 2.5 ppm, which has a line width of ~ 10 - 22 Hz is much less broadened compared with that of the methylene protons. The signal of the phenyl group is broadened from ~ 10 - 26 Hz in the free ligand to ~ 62 - 80 Hz in the complexes.

Although the n.m.r. spectral evidence of the present system is not as strong as that in the (ethylthio)acetic acid, the larger broadening effect observed in the methylene group and the phenyl group compared with that of the methyl group seems to support that chelate formation does occur in these complexes. The species in the solution may be still partially coordinated to the ligand.

F. Conclusion

From the above discussion, it is shown that these copper(II) complexes are magnetically dilute with $d_{x^2-y^2}$ (or d_{xy}) ground state. Their electronic spectra indicate a possibility of a distorted octahedron or a compressed tetrahedral or a square coplanar. There is no unequivocal evidence from the infrared spectra to support the involvement of sulfur and selenium atoms in these complexes.

The physical properties of these copper(II) complexes are comparable with those of bis(phenoxyacetato)copper(II)dihydrate in which chelation by the (phenoxy)acetato ligand has been established by x-ray study.¹⁵¹ The stability constants show that the thio-ligands form more stable complexes

Table 19
¹H n.m.r. Spectra of Copper(II) Complexes^a

| Compound | Chemical Shift (ppm) | | |
|--|--------------------------------|-----------------|-------------------------------|
| | RC ₂ H ₄ | CH ₂ | CH ₃ and DMSO |
| (Ph-SA) ₂ Cu | 6.67 (-68Hz) ^b | ? | -- |
| (p-CH ₃ -SA) ₂ Cu | 6.66 (-62Hz) | ? | 2.55 (-14Hz) ^c |
| (m-CH ₃ -SA) ₂ Cu | 7.40 (-74Hz) | ? | 2.60 (-14Hz) ^c |
| (p-CH ₃ -SeA) ₂ Cu | 6.33 (-80Hz) | ? | 2.50 |
| p-CH ₃ -SAH ^d | 7.20 (-26Hz) | 3.58 (2Hz) | 1.75 (-40Hz) 2.30 (-2.5Hz) |

^a ¹H n.m.r. spectra were measured in δ₆-DMSO.

^b Line width at half-height.

^c Methyl group and DMSO absorption.

^d ¹H n.m.r. spectrum of parent acid in CDCl₃.

than the oxy-ligands. 123,124

135

Since the magnetic moments of these complexes are normal, they may be polynuclear six-coordinate derivatives with bridging carboxyl groups. The bridge, being in an anti-anti configuration,¹⁵² holds the copper atoms too far apart for any interaction to occur. With the informations available, the possibility of stereochemistries for four-coordination for these complexes cannot be ignored. Regular tetrahedral copper(II) systems are uncommon and the tetrahedron, if present, may be a compressed tetrahedral structure (ground state d_{xy}). To the extreme of distortion of elongated tetragonal structure or of compressed tetrahedral structure, a square coplanar structure is also possible.

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APPENDIX

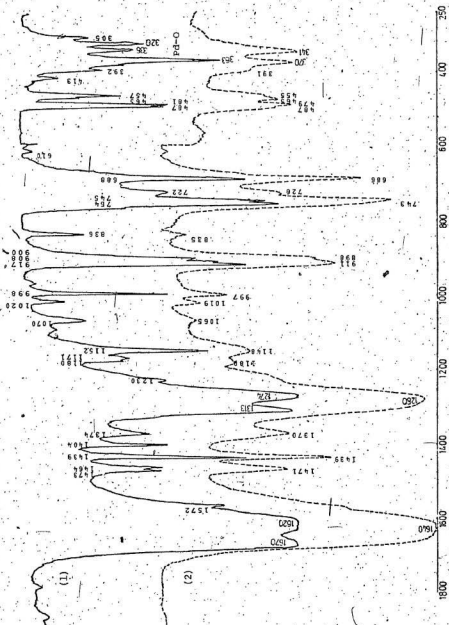
Magnetic Moments

The magnetic susceptibilities of the bis-complexes of copper(II) were obtained by the Faraday or Gouy method at room temperature. Mercury(II) (tetrathiocyanato)cobaltate(II), $\text{Hg}(\text{Co}(\text{CNS})_4)_2$, was used as the calibrant. The data collected are as follows.

| Compounds | $\chi_g (10^{-6}) \text{ cgs}$ | $\chi_M^{\text{corr}} (10^{-6}) \text{ cgs}$ | $\mu_{\text{eff}} (\text{B.M.})$ |
|--|--------------------------------|--|----------------------------------|
| $(\text{Ph-SA})_2\text{Cu}^a$ | 3.426 | 1542 | 1.932 |
| $(p\text{-CH}_3\text{-SA})_2\text{Cu}^b$ | 2.789 | 1411 | 1.832 |
| $(m\text{-CH}_3\text{-SA})_2\text{Cu}^a$ | 3.662 | 1760 | 2.060 |
| $(p\text{-CH}_3\text{-SeA})_2\text{Cu}$ | 2.169 | 1346 | 1.803 |

a By Faraday method.

b By Gouy method.

Fig. 10a Infrared Spectra of (1) $(\text{Ph-SA})_2\text{Pd}$ and (2) $(\text{Ph-SA})_2\text{Pd} \cdot \text{H}_2\text{O}$.

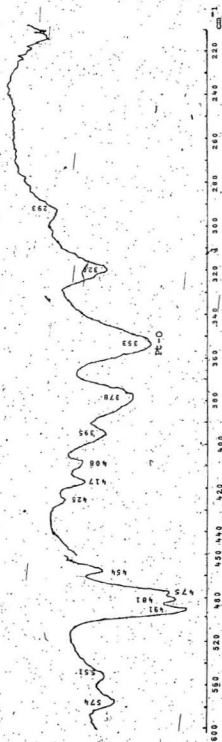


Fig. 10b - Infrared Spectrum ($600\text{-}200\text{ cm}^{-1}$) of $(\text{Ph-SN})_2\text{Pt}$.

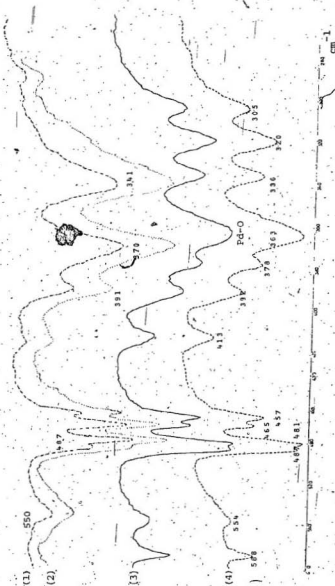


Fig. 10c. Infrared Spectra ($600\text{--}200\text{ cm}^{-1}$) of $(\text{Ph-SA})_2\text{Pd}\cdot 4\text{H}_2\text{O}$ (1) initial reaction product (2) product recrystallized from water; of $(\text{Ph-SA})_2\text{Pd}$ (3) product recrystallized from dichloroethane and (4) product recrystallized from methanol.

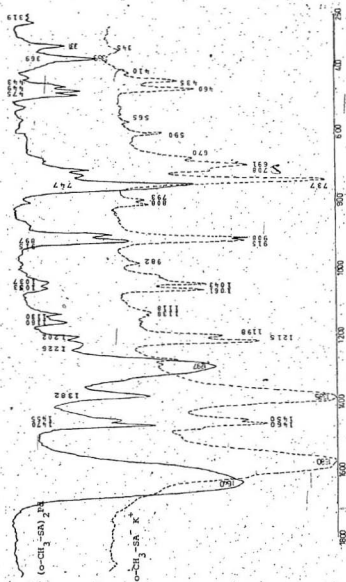
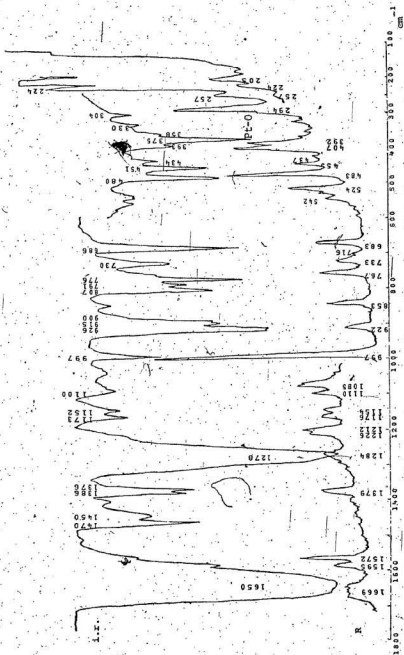


Fig. 10d Infrared spectra of (o-CH₃-SA)₂Pa and its free ion o-CH₃-SA⁻ K⁺.

Fig. 10e Infrared and Raman Spectra of (m-CH₃)₂Pt.

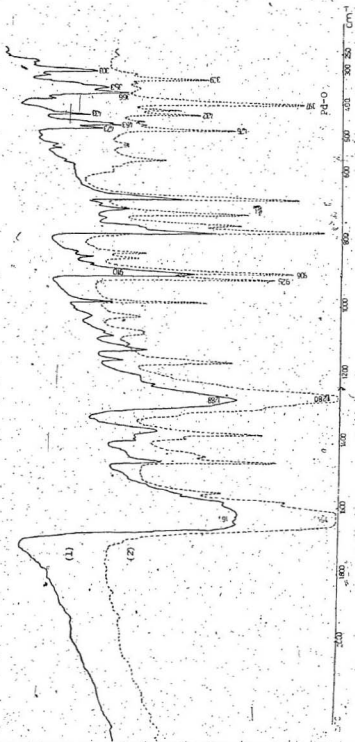


Fig. 10f Infrared Spectra of (1) $(m\text{-CH}_3\text{-SA})_2\text{Pd.H}_2\text{O}$ and (2) $(m\text{-CH}_3\text{-SA})_2\text{Pd}$.

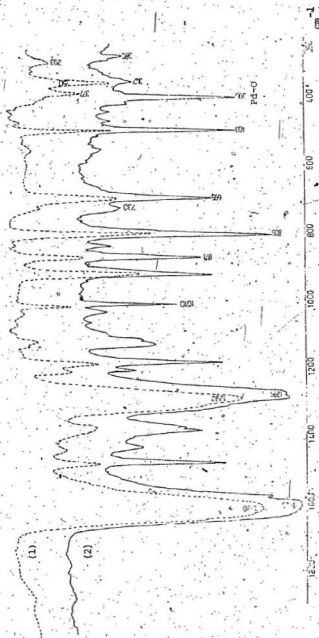


Fig. 109 Infrared Spectra of $(p\text{-CH}_3\text{-Sea})_2\text{Pd.H}_2\text{O}$ (1) and $(p\text{-CH}_3\text{-Sea})_2\text{Pd}$ (2).

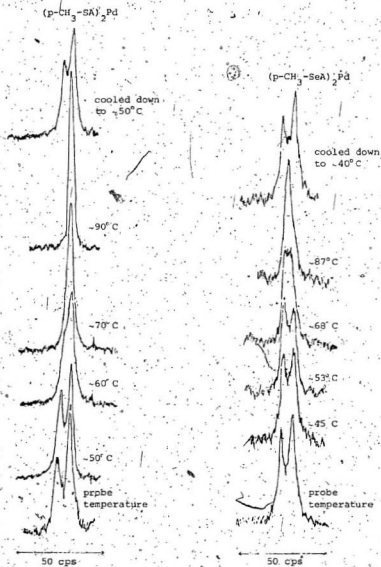


Fig. 11a 60 MHz ^1H n.m.r. spectra of the methyl groups of $(p\text{-CH}_3\text{-SA})_2\text{Pd}$ and $(p\text{-CH}_3\text{-SeA})_2\text{Pd}$ in 1,1,2,2-tetrachloroethane at various temperatures.

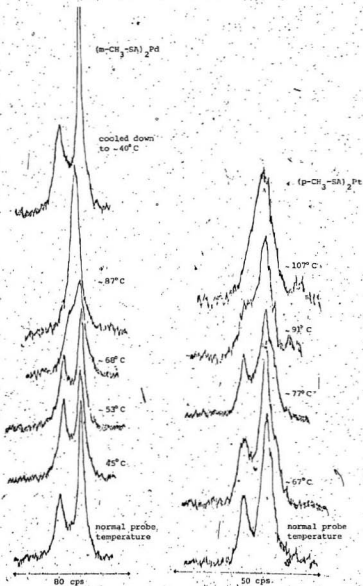


Fig. 11b 60 MHz ^1H -n.m.r. spectra of the methyl groups of $(m\text{-CH}_3\text{-SA})_2\text{Pd}$ and $(p\text{-CH}_3\text{-SA})_2\text{Pt}$ in 1,1,2,2-tetrachloroethane at various temperatures.

Fig. 11c 100 MHz (Low Temperature) ^1H n.m.r. Studies of $(\text{p-CH}_3\text{-SA})_2\text{Pt}$
in CD_2Cl_2 . (* downfield from TMS in cps)

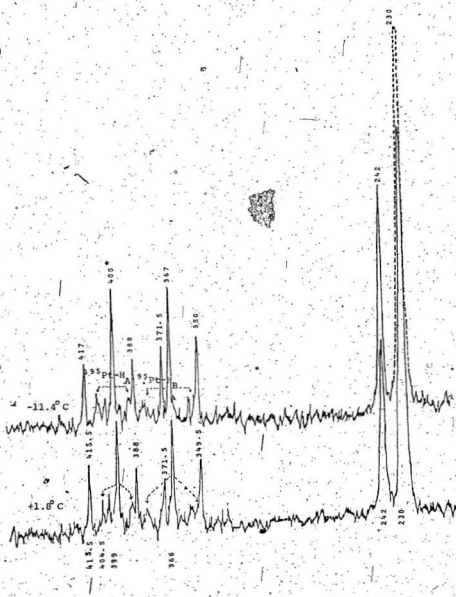
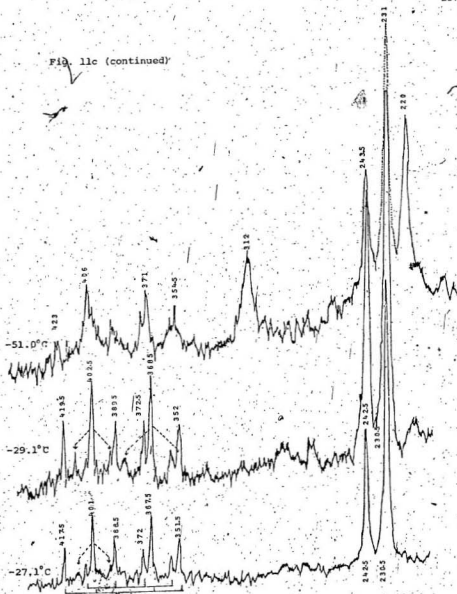


Fig. 11c (continued)



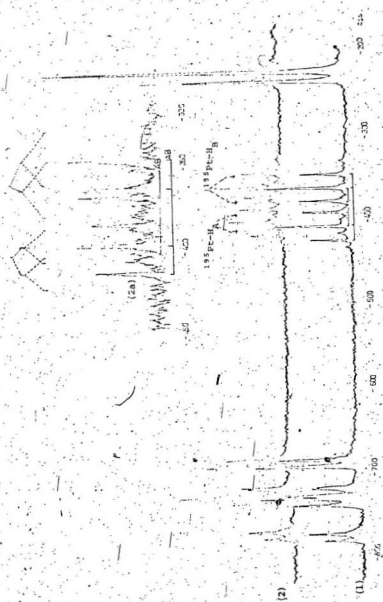


Fig. 11. 100 MHz ^1H n.m.r. spectra of $(\text{p-CH}_3\text{-SA})_2\text{Pt}$ of (1) product from reaction of 1:1 metal-ligand ratio in CDCl_3 and (2) product from reaction of 1:2 metal-ligand ratio in CDCl_3 and (2a) in CDCl_2 at -22°C .

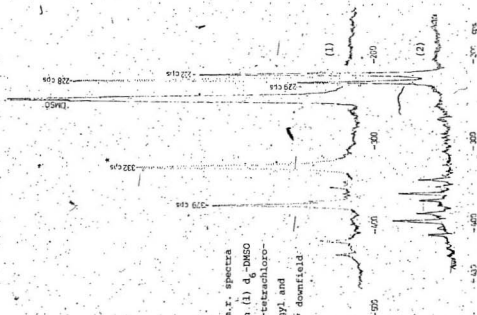


Fig. 12a 100MHz ^1H n.m.r. spectra of $(o\text{-CH}_3)_2\text{Pt}$ in (1) D_2O and (2) in 1,1,2,2-tetrachloroethane for the methyl and methylene region. (* downfield from TMS)

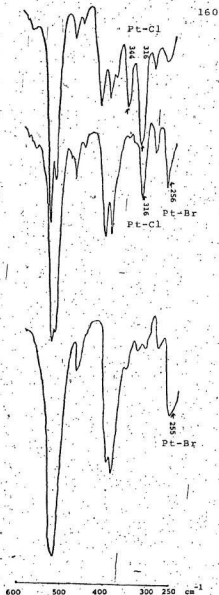


Fig. 16a Infrared spectra of (1) $\text{K}[\text{Pt}(\text{p-CH}_3\text{-SO-A})\text{Cl}_2]$,
 (2) $\text{K}[\text{Pt}(\text{p-CH}_3\text{-SO-A})\text{ClBr}]$ and (3) $\text{K}[\text{Pt}(\text{p-CH}_3\text{-SO-A})\text{Br}_2]$
 in the region ($600\text{-}250\text{ cm}^{-1}$).



